

Corrosion Behavior of 3D Printed 316 L Stainless Steel IN Chloride and Hydrocarbon Environments

BY
Ibrahim Awad Albalawi

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

Material Science and Engineering

MAY 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA ,

DEANSHIP OF GRADUATE STUDIES

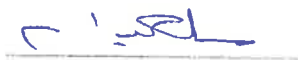
This thesis, written by **Ibrahim Awad Albalawi** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN MATERIALS SCIENCE & ENGINEERING**.



Dr. Turki N. Baroud
Department Chairman



Dr. Ahmad A. Sorour
(Advisor)



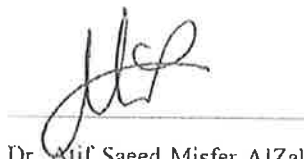
Dr. Suliman S. Al-homidan
Dean of Graduate Studies



Dr. Ihsan Ul Haq Toor
(Member)

6-12-2023

Date



Dr. Aliif Saeed Misfer AlZahrani
(Member)



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2023

Dedication

To My Family

ACKNOWLEDGMENTS

First, I would like to thank God almighty for allowing me to finish this thesis, then my parents, my wife, my son Saud, and the rest of my family for giving me support and encouragement in my work and studies. I am also grateful to my thesis advisor, Dr. Ahmad Sorour, for his guidance and expertise throughout the research process, as well as to my colleagues and friends especially Dr. Abdulrahman Al-Sayel who provided valuable feedback and insights. Furthermore, I would like to thank Dr. Akeem Adesina for his valuable guidance and effort with the synthesis and subsequent experiments and tests, with the help of Allah, to achieve our desired objectives.

I would also like to thank the committee members, Dr. Ihsan Ul Haq Toor and Dr. Atif Saeed AlZahrani, for their valuable involvement and comments. Without their help, this thesis would not have been possible. I hope that my research will contribute to the field and inspire others to continue exploring this topic. Finally, thanks to King Fahd University of Petroleum & Minerals (KFUPM) in Dhahran and its Research Institute (RI) especially the Research Center for Advanced Materials for creating and providing support throughout the project's completion.

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LIST OF ABBREVIATIONS

AM	:	Additively Manufacturing
AMed	:	Additively Manufactured
SLM	:	Selective Laser Melting
SS	:	Stainless Steel
SEM	:	Scanning Electron Microscopy
EDS	:	Energy-dispersive X-ray Spectroscopy
XRD	:	X-ray diffraction
EDX	:	Energy dispersive spectroscopy
CPDP	:	Cyclic Potentiodynamic Polarization Megapascals
EIS	:	Electrochemical Impedance Spectroscopy
OCP	:	Open Circuit Potential
LPR	:	Linear Polarization Resistance
μm	:	Micro-meter
mpy	:	Mils per year

ABSTRACT

Full Name : [Ibrahim Awad Albalawi]

Thesis Title : [CORROSION BEHAVIOR OF 3D PRINTED 316 L STAINLESS STEEL
IN CHLORIDE AND HYDROCARBON ENVIRONMENTS]

Major Field : [Material Science and Engineering]

Date of Degree : [April 2023]

Additive Manufacturing or 3D printing is one of the most promising technologies that can be utilized in the oil and gas industry, particularly for manufacturing alloy and stainless-steel components. In this regard, 316L stainless steel is frequently utilized and can be conveniently manufactured using selective laser melting (SLM). This study examines the electrochemical behavior of 316L stainless steel fabricated by selective laser melting (SLM) with varying energy densities and compares it with that of wrought stainless steel. The electrochemical measurements were conducted at room temperature in a 3.5 wt.% NaCl solution with four pH levels. In addition, the electrochemical measurements were conducted at temperature of 70 C in a 3.5 wt.% NaCl solution and pH 1 to simulate the aggressive industry environment in the brine water system in the crude unit. The 316L SLMed stainless steel and the wrought samples were immersion in 3.5% NaCl and crude oil (hydrocarbon) for 14 days at room temperature. An optical profilometer was used to measure and evaluate the pitting corrosion of the samples that were immersed. The corrosion analysis was carried out using Linear Polarization Resistance (LPR), Potentiodynamic Polarization (PDP), open circuit potential (OCP), and Electrochemical impedance spectroscopy (EIS). Moreover, an electron

microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and an x-ray diffractometer was used to carry out the microstructure investigation (XRD). The pitting resistance of the 3D printed sample was greater than that of the wrought alloy, particularly at pH 1, where the E_{pit} values of the samples demonstrate a distinct difference. The immersion test observed that the samples immersed in crude had a higher pit density than the samples immersed in 3.5% NaCl solution, indicating that a lower corrosion rate resulted in a higher pit density and lower pit depth and pit size. The calculated thickness of the passivation layer shows that SLM samples have a slightly thicker passivity film than wrought samples. Corrosion rate and corrosion potential did not vary significantly between the samples but still shows that the 3D printed samples are better.

Keywords: 3D printing, additive manufacturing, selective laser melting, corrosion, 316L stainless steel

ملخص الرسالة

الاسم الكامل: إبراهيم عوض سليمان البلوي

عنوان الرسالة: سلوك التآكل من الفولاذ المقاوم للصدأ L316 المطبوع ثلاثي الأبعاد بواسطة ذوبان الليزر الانتقائي (SLM) في بيئات الكلوريد والهيدروكربون

التخصص: هندسة وعلم المواد

تاريخ الدرجة العلمية: مارس 2023

يُعد التصنيع الإضافي أو الطباعة ثلاثية الأبعاد من أكثر التقنيات الواعدة التي يمكن استخدامها في صناعة النفط والغاز ، لا سيما في صناعة مكونات السبائك والفولاذ المقاوم للصدأ. في هذا الصدد ، يتم استخدام الفولاذ المقاوم للصدأ L316 بشكل متكرر ويمكن تصنيعه بسهولة باستخدام الصهر الانتقائي بالليزر (SLM). تبحث هذه الدراسة في السلوك الكهروكيميائي للفولاذ المقاوم للصدأ 316L الناتج عن الذوبان الانتقائي بالليزر (SLM) بكثافات طاقة متفاوتة ومقارنته بسلوك الفولاذ المقاوم للصدأ التقليدي. أجريت القياسات الكهروكيميائية في درجة حرارة الغرفة في محلول كلوريد الصوديوم 3.5٪ بالوزن مع أربعة مستويات من الأس الهيدروجيني. بالإضافة إلى ذلك ، أجريت القياسات الكهروكيميائية عند درجة حرارة 70 درجة مئوية في محلول كلوريد الصوديوم بنسبة 3.5٪ بالوزن ودرجة الحموضة 1 لمحاكاة بيئة الصناعة العدوانية في نظام المياه المالحة في الوحدة الخام. تم غمر الفولاذ المقاوم للصدأ L SLMed316 والعينات التقليدية في 3.5٪ كلوريد الصوديوم والزيت الخام (الهيدروكربون) لمدة 14 يومًا عند درجة حرارة الغرفة. تم التحكم في الأس الهيدروجيني عن طريق إضافة قطرات حمض الهيدروكلوريك في 3.5٪ كلوريد الصوديوم والزيت الخام حتى يتم تقليل الأس الهيدروجيني ليكون الرقم الهيدروجيني 1. تم استخدام مقياس التشكيل البصري لقياس وتقييم تآكل التنقر للعينات التي تم غمرها. تم تقييم كثافة الحفرة ، عمق الحفرة الأقصى ، متوسط عمق الحفرة وحجم الحفرة لكل عينة. تم إجراء تحليل التآكل باستخدام مقاومة الاستقطاب الخطي (LPR) ، والاستقطاب الديناميكي الديناميكي (PDP) ، وإمكانات الدائرة المفتوحة (OCP) ، والتحليل الطيفي للمقاومة الكهروكيميائية (EIS). علاوة على ذلك ، تم استخدام مجهر

إلكتروني (SEM) مجهز بمطياف الأشعة السينية المشتت للطاقة (EDS) ومقياس حيود الأشعة السينية لإجراء فحص البنية المجهرية (XRD). كانت مقاومة التنقر للعينات المطبوعة ثلاثية الأبعاد أكبر من مقاومة السبائك التقليدية ، خاصة عند الرقم الهيدروجيني 1 ، حيث تُظهر قيم Epit للعينات اختلافاً واضحاً. تُظهر السماكة المحسوبة لطبقة التخميل أن عينات SLM لها فيلم سلبي أكثر سمكاً قليلاً من العينات التقليدية. لاحظ اختبار الغمر أن العينات المغمورة في الخام كانت ذات كثافة حفرة أعلى من العينات المغمورة في محلول كلوريد الصوديوم بنسبة 3.5٪ ، مما يشير إلى أن معدل التآكل المنخفض أدى إلى زيادة كثافة الحفرة وانخفاض عمق الحفرة وحجمها. لم يختلف معدل التآكل وإمكانية التآكل بشكل كبير بين العينات ولكن لا يزال يُظهر أن العينات المطبوعة ثلاثية الأبعاد أفضل.

الكلمات الرئيسية: الطباعة ثلاثية الأبعاد ، التصنيع الإضافي ، الصهر الانتقائي بالليزر ، التآكل ، الفولاذ المقاوم للصدأ

L316

CHAPTER 1 INTRODUCTION

Corrosion is a major issue in the oil and gas industry, compromising integrity and increasing operating costs. It results from the interaction of metal with the corrosive environment, which can lead to leaks, explosions, and other safety risks. To make sure operations are safe and run well, it is important to take steps to control corrosion. One of these steps is to use a corrosion-resistant material instead of carbon steel. Because of its low cost and excellent corrosion resistance, 316L stainless steel is one of the best materials used in the oil and gas industry. Designing, mold making, melting, casting, cutting, machining, and finishing are all steps in the traditional manufacturing of 316L stainless steel [1]. These steps will take a long time, in addition to logistical and transportation time. Moreover, traditional manufacturing has energy consumption and high mass loss due to machining. However, new metal additive manufacturing (AM), also known as "3D printing", technology can solve these problems and bridge the gap between the manufacturer and the industry. AM is the most cost-effective method of producing small to medium-sized objects with intricate shapes and geometries. As illustrated in Figure 1, it requires less processing time, has a comparable cost, and has fewer manufacturing stages compared to the traditional manufacturing [2]. AM differs from traditional material removal processes like milling and turning due to its incremental addition way of part development during the manufacturing process, rather than the traditional method of removing chips from a block of material [3].

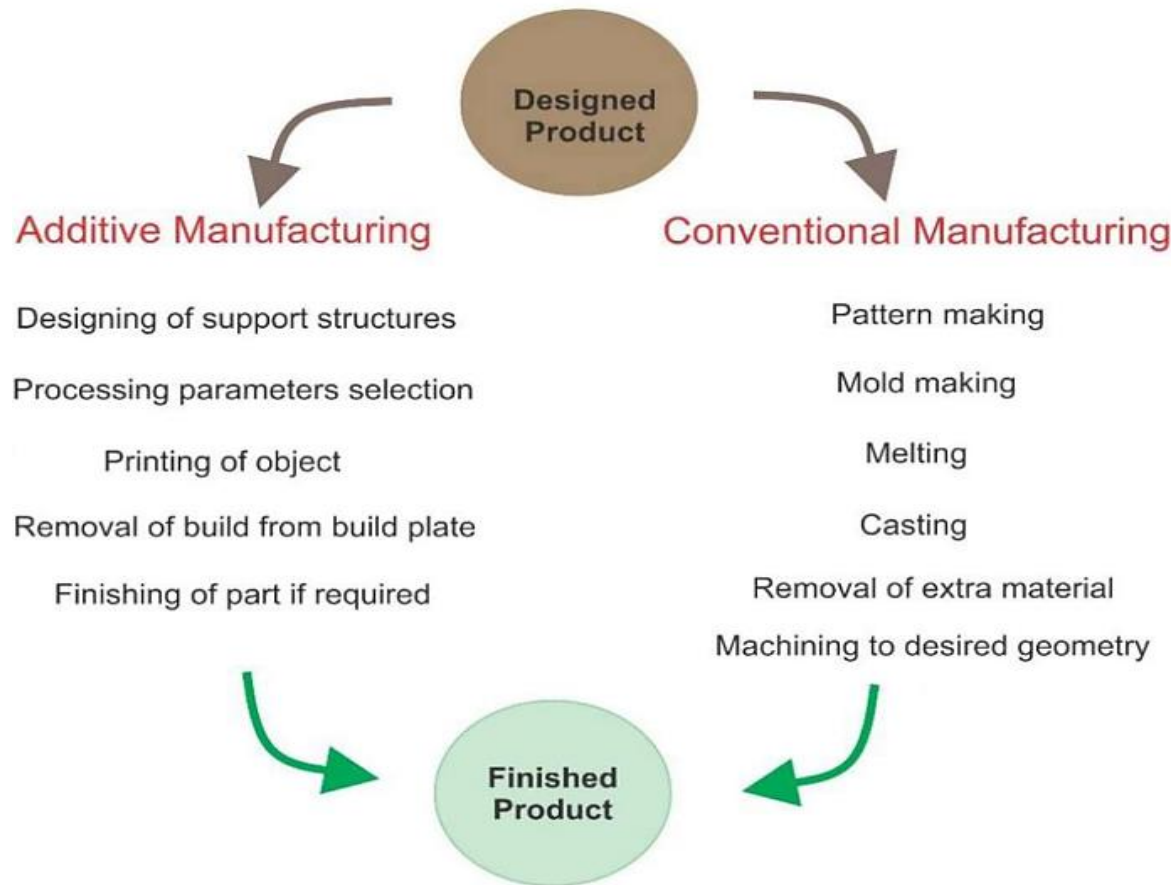


Figure 1 A comparison of traditional and additive manufacturing [1]

One of the potential AM technologies is the Selective Laser Melting (SLM). It was developed in 1995 in Germany and also named the direct metal melting (DMM) or laser-based powder bed fusion (LPBF) [4]. Because of its adaptability and potential for quick manufacture, SLM is a regularly used for fabricating metal parts [5] [6]. Using a high-energy laser beam to fuse together a thin layer of metal particles on a flatbed, the SLM method builds up metal structures layer by layer [7], [8]. SLM-produced parts have decreased density and high porosity, and some metals exhibit poor corrosion performance due to porosity [9]. However, it was observed that the scan

speed has a significant influence on the porosity [10]. Additionally, it has been demonstrated that the energy density, layer thickness and laser power have an influence on the relative density and mechanical properties of the fabricated metal by SLM [11]. To the authors' knowledge, however, there hasn't been any published research on the impact of porosity and energy density on the corrosion of 316L stainless steel produced by AM in hydrocarbon environment. In this regard, the relationship between energy density and porosity and their effect on corrosion will be studied and explained in the upcoming section of this study.

In recent years, the use of SLM for the fabrication of stainless steel parts has received considerable attention [12]. stainless steel is an iron-based alloy composed of chromium along with other components in specific proportions. Among these, 316L grade is the second most common austenitic stainless steel after 304/A2. The general composition of a 316L alloy are Fe – 16 Cr – 12 Ni – 3 Mo [5] [13]. Considering its importance, several research studies have focused on fabricating 316L stainless steel parts by using the SLM technique and analyzed a variety of their characteristics such as microstructure, mechanical properties, and corrosion resistance in acidic environments. Yet, there is a dearth of research on the low energy density in acidity solutions and the simulation of acid environment and temperature in the industry. Therefore, further research is needed to investigate the effects of low energy density of acidity solutions on the microstructure and mechanical properties of 316L stainless steel parts fabricated by SLM technique, as well as to simulate the acid environment and temperature in the industry for a better understanding of their corrosion behavior.

CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

2.1 316L stainless steel.

Stainless steels play a key role in the modern world, even though they only make up about 2% of total steel production [14]. Stainless steel is a type of steel alloy that contains at least 10.5% chromium, which makes it highly resistant to corrosion and rust [15]. Stainless steel is widely used in various industries, such as construction, automotive, and medical equipment, due to its durability and hygiene. In oil and gas applications, austenitic stainless steels like 304 and 316 are commonly used due to their high corrosion resistance and ability to withstand high temperatures and pressures[16].

Based on the matrix phase(s), stainless steels can be divided into austenitic, martensitic, ferritic, and duplex [17] . Austenitic stainless steels are non-magnetic and have excellent corrosion resistance, while martensitic stainless steels are magnetic and have high strength. Ferritic stainless steels have good corrosion resistance but lower toughness, and duplex stainless steels have a combination of both austenitic and ferritic properties. The austenitic stainless steel 316L is commonly used in the oil and gas industries and has many applications [18]. It is used in heat exchangers, pipelines, pressure vessels, and rotating equipment such as pumps and compressors, etc., to provide good corrosion resistance in the industrial corrosive environment and increase the equipment's life. Additionally, its low carbon content makes it suitable for welding and fabrication.

Stainless steel can be easily fabricated into different shapes and sizes, making it a versatile material for different applications. Conventional methods to fabricate 316L stainless steel include casting, forging, and welding. These methods have some disadvantages, such as poor material properties,

long production times and high costs [19]. Additionally, the conventional methods for fabricating 316L stainless steel can also lead to material waste, poor working environment with high temperature, high labor intensity and others environmental concerns. Moreover, it forces the industry to have additional indirect costs and land space to store the material and make it available when it is needed.

As a solution, additive manufacturing has become a promising way to make 316L stainless steel because it improves the material's properties, cuts down on production time, and costs less. Additive manufacturing also minimizes material waste and environmental impact by using only the necessary amount of material to create the desired shape. More additive manufacturing advantages will be discussed in detail in the coming sections.

2.2 Additive Manufacturing

In 1987, stereolithography (SLA) from 3D Systems brought about the emergence of AM, which used a laser to solidify thin layers of ultraviolet light-sensitive liquid polymers. In the late 1980s, several new AM technologies began to emerge. These included selective laser sintering (SLS), developed by Carl Deckard, and fused deposition modeling (FDM), developed by S. Scott. The 1990s saw the development of many new technologies including direct metal laser sintering (DMLS) and binder jetting [20].

In the 2000s, the development of bioprinting using AM revolutionized the medical field by making it possible for scientists to create custom, patient-specific medical devices. As AM machines became more affordable, they started to be used in both research and production settings. Modern AM techniques have enabled businesses to produce more complex and accurate end parts than

ever before, which has made prototyping unnecessary. In this way, customization is now more accessible and affordable, so businesses can offer customers more personalized options [21].

2.2.1 Types of AM Technologies

There are many types and technologies of AM. Some are used for nonmetallic parts, while others are used for metallic parts. The main types are material extrusion, vat photopolymerization, sheet lamination, powder bed fusion, binder jet, and laser selective melting. Material extrusion involves melting and depositing material layer by layer, while vat photopolymerization uses a liquid resin that is hardened by a light source. Material extrusion is a common AM process that uses a nozzle or hole to push material out and make parts with multiple layers [22] [23]. Printed parts are not as dense as injection-molded parts and have issues with repeatability due to printer characteristics or printing conditions. [24]. Vat photopolymerization triggers the polymerization reaction, forming chains of polymers or crosslinks to form a solid resin. [25]. Sheet lamination (SHL) is an AM technique that has been used for more than fifty years, initially to make patterns on paper but since expanding to polymers and metals. It involves cutting, stacking, and bonding materials to form an object that cannot be reused and is typically discarded [26], [27]. Powder bed fusion is an AM melting process that produces parts from powdered metal by fusing it using a heat source. The powder around the solidified portion serves as a support for any overhanging features [28]. Binder jetting is a powder bed AM process that uses binders to glue powder together instead of sintering in a furnace [29]. Binder jetting is a multi-step process that can be used to create 3D parts from powdered materials, but it requires post-processing steps and has higher surface roughness and lower resolution than other additive manufacturing methods [30]. Finally, The selective laser

melting technique (SLM) is an advanced AM technique that uses a high-power laser to melt and fuse powdered metals. This technique will be discussed in detail in the coming sections and used in this study.

2.2.2 Materials for AM

AM can be used to make parts from a variety of materials such as plastics, metals, ceramics, composites, and concrete. Modern AM printers are now capable of taking a range of similar materials to create multi-material components. For example, a toothbrush having a stiff handle with softer areas to give additional grip can be conveniently produced. The capacity to print with an array of materials and sometimes combine different materials into one part continues to evolve [31].

Metal AM, where components are created from metal, is now becoming a focal point for many industries due to its tool-free and speedy production of custom parts. This raises the question of whether rapid prototyping can also become rapid manufacturing. However, before additively manufactured metals (AMed), metal parts are frequently used in the industry for bulk production, their material characteristics must meet or surpass the qualities of materials produced through traditional manufacturing methods [21].

2.2.3 Advantages of AM Technique

The first challenge of manufacturing is overcoming the inherent difficulty of creating something from scratch. 3D printers excel at this task, as they can produce an object from a 3D file and have a great deal of flexibility in how they do it. They were first used to make rapid prototypes or items that could be produced quickly and easily for testing purposes. Some of the important advantages

of 3D printing for meatal parts are discussed as follows [31],

- AM enables manufacturers and industries to create complex structures that cannot be fabricated conveniently by using molds or castings. For products that are customized and personalized, such rotating parts of the pump, impellers and complex geometry parts, AM can be used to make parts with slight changes without needing to make molds.
- One of the most important benefits of AM for the industry is that 3D printing can solve the problem of materials and parts not being available and cut down on the time it takes to move things around. Particularly important for an industry that is in a remote area, the logistics of transporting materials and equipment can be challenging. Additionally, 3D printing allows for on-demand production, reducing the need for large inventories and storage space.
- 3D printers are increasingly being used to make parts from a wide variety of materials. The ability to change the composition of materials, including by mixing them, makes it possible to put high-performance materials at a desired place like surfaces or edges. This capability also allows people to customize parts for their needs with temperature or corrosion resistance properties.
- Most of the indirect costs can be eliminated with 3D printers, such as the time it takes to get the materials, the cost of logistics, and the cost of storing them. They can also keep the materials from getting damaged while they are being stored. This makes 3D printing a cost-effective and efficient solution for manufacturing small

batches of customized products. Additionally, it allows for faster prototyping and product development cycles.

- 3D printing technology can also reduce the environmental impact of traditional manufacturing processes by minimizing waste and using eco-friendly materials. This makes it a more sustainable option for businesses looking to reduce their carbon footprint.

Finally, it is worth mentioning here that the AM stainless steel has a promising future in the oil and gas industries and can be used instead of stainless steel materials manufactured with conventional methods. Its unique manufacturing process allows for greater design flexibility and the ability to create complex geometries. Additionally, AM stainless steel exhibits improved mechanical properties, such as higher strength and corrosion resistance, making it an ideal choice for demanding applications in the oil and gas industries.

2.3 Selective Laser Melting

The selective laser melting technique (SLM), also known as direct metal laser melting (DMLM), is an advanced AM technique that uses a high-power laser to melt and fuse powdered metals. With SLM technology, complex geometries can be manufactured that are not possible with conventional manufacturing methods ranging from casting to forging, and powder metallurgy [4]. A general schematic of the SLM process is shown in figure 2.

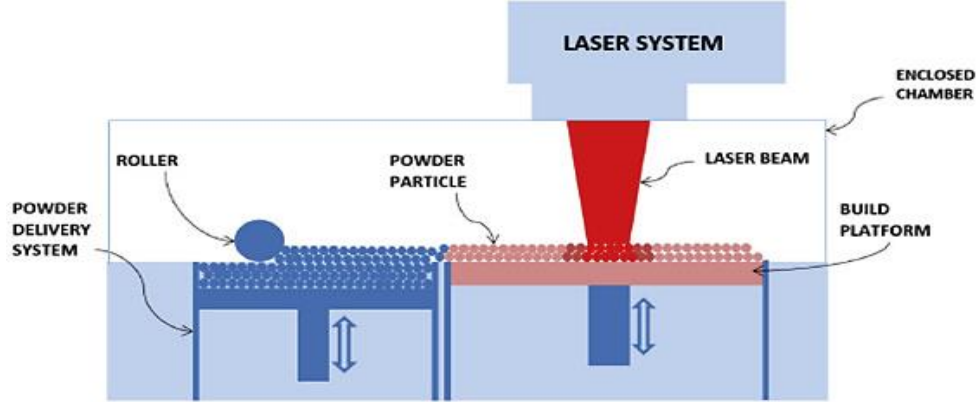


Figure 2 The schematic of an SLM process [32]

Initially, a 3D computer-assisted drawing file (user-defined) of the part is divided into layers based on layer thickness to form a layered material. As shown in the figure 2, the powdered raw material is applied to a substrate plate followed by melting and fusion using a high-power laser. During the process, several parameters are responsible for imparting the respective properties to the fabricated part. These parameters define the amount of energy consumed by a unit volume of the fabricated part. It is often referred to as energy density (E_d) and is given by the relation,

$$E_d = \frac{P_{laser}}{v_{scan} S_{hatch} t_{layer}} \quad (1.1)$$

In the above equation, P_{laser} is the power of the laser in W, v_{scan} is the scanning speed in mm/s, S_{hatch} is the hatch spacing in mm, and t_{layer} is the thickness of the layer in mm. The structural properties and functional characteristics of the fabricated part are directly dependent on the selection of the energy density and related parameters [4] [32]. The SLM process has been widely used for the fabrication of parts using 316L stainless steel and is further discussed in subsequent sections.

2.4 SLM for 316L Stainless Steels

In SLM-based manufacturing, a high energy density may be employed to create materials with a density greater than 99.8%. It has been demonstrated earlier that certain combinations, namely a small hatch spacing, and a quick scan speed, result in the manufacture of materials with a high density [33]. In most cases, the presence of porosity may lead to localized corrosion in SLMed 316L [34], [35]. Corrosion behavior has been researched as a function of the key laser parameters (laser power and scan speed), which significantly affect the material's pores. This will be discussed in the upcoming sections.

The SLM can be conveniently used to produce metallic parts by using stainless steel feedstock powder. The 316L is one of the most frequently used alloys in metallic-based SLM processes. SLM-fabricated (SLMed) 316L stainless steel parts experience enhancement in properties such as strength, work hardening, and corrosion resistance. During manufacturing, the high scanning speed of the laser enables short exposure to the powder bed leading to rapid melting and solidification side-by-side [36] [37] as shown in figure 3

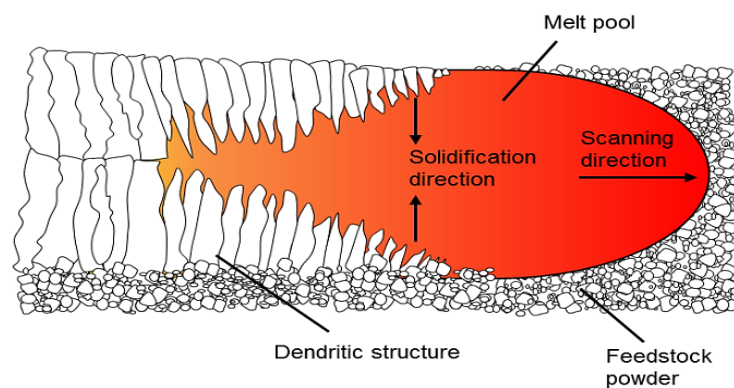


Figure 3 An illustration of melting and solidification of stainless steel in SLM [37]

Here, the rate of cooling and geometry of the melt container directly influences the microstructure and grain growth in the produced part. For example, 316L stainless steel components fabricated using SLM typically experience higher cooling rates leading to a microstructure having finely graded cells with a diameter of $\sim 1\mu\text{m}$ and columns with sizes up to $100\mu\text{m}$. Whereas, in the case of wrought 316L, an equiaxed coarse structure having sharp boundaries of grains is usually obtained [1]. A comparison of the structures is shown in figure 4. The SLMed 316L stainless steel samples constitute a distinctive microstructure that results in improved mechanical and corrosion properties [1] [5]. The published literature in this regard shows that the microstructures of SLMed 316L parts are largely dependent upon processing parameters. These studies are further elaborated on in the next sections.

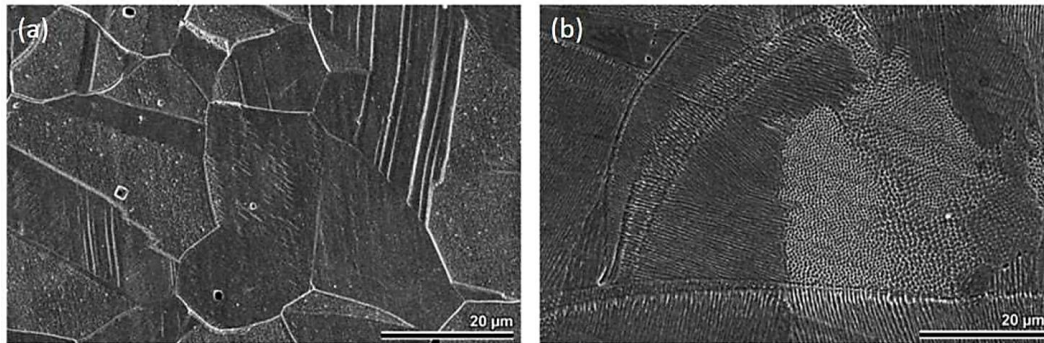


Figure 4 A comparison of the microstructures of 316L stainless steel (a) wrought vs (b)

SLMed 316L stainless steel [1]

2.5 Microstructure of SLMed 316L Stainless Steel

In SLMed 316L stainless steel, the hierarchical macro, micro, and nanoscale structures are produced. In this regard, a thorough investigation was carried out on the effect of process variables

on the microstructure of SLMed 316L stainless steel [38]. Likewise, the physical and mechanical characteristics of SLM materials can be impacted by the processing parameters, such as laser power, scan speed, layer thickness, and hatch spacing [33]. At the macroscale, the SLM process causes the creation of overlapping melt pools with a semicircular shape in the plane perpendicular to the direction of construction.

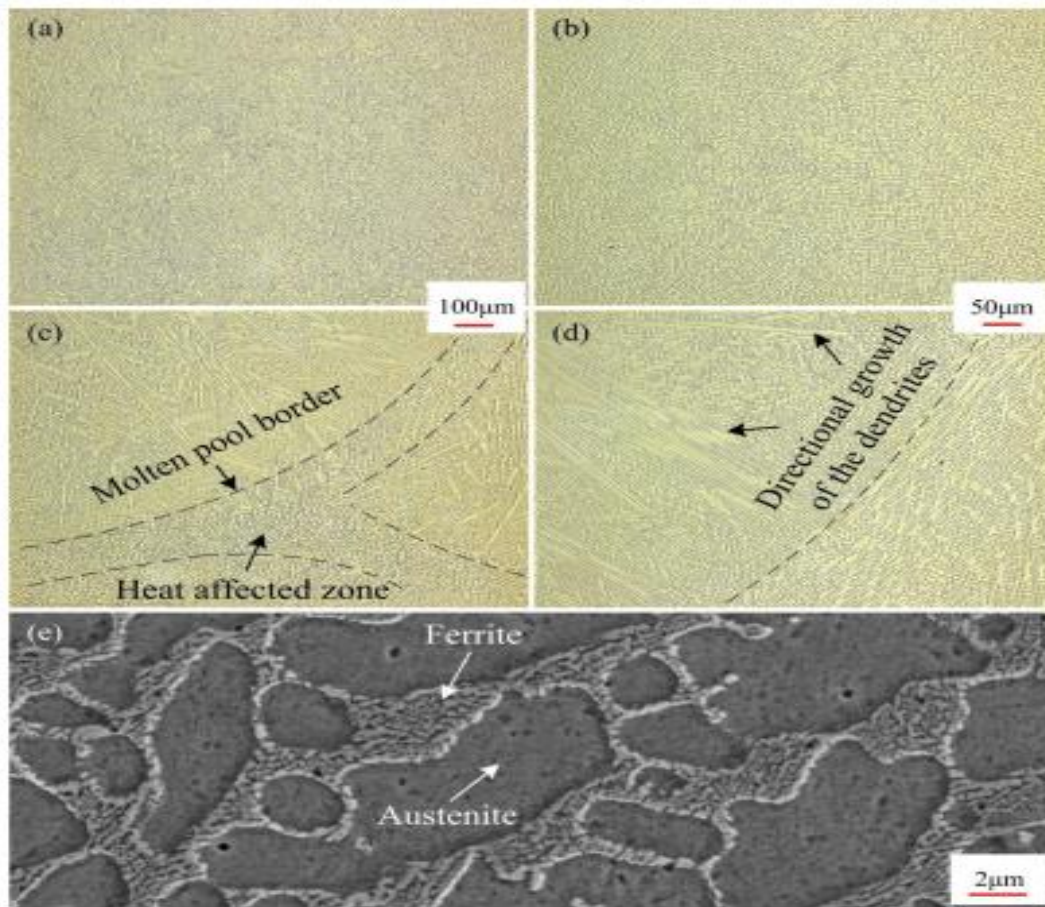


Figure 5: SLMed 316L stainless steels at different building directions, (a) and (b) the building direction of 0°, (c) and (d) the building direction of 90°, (e) enlarged view of the microstructure corresponding to (b).[39]

Figure 5 shows SLMed 316L stainless steel fabricated by using different building direction. It was

found that the building direction (the laser scanning directly) influenced the microstructure of the samples exhibiting a cellular dendritic configuration [39]. Figure 5 (e) shows the austenite and ferrite phase in the SLMed 316L stainless steel. The austenitic phase is the main component, however, SLMed 316L stainless steel also contains residues of ferrite. In some instances, the complex subgrain structure of this steel's alloying components is noted to be distributed unevenly.

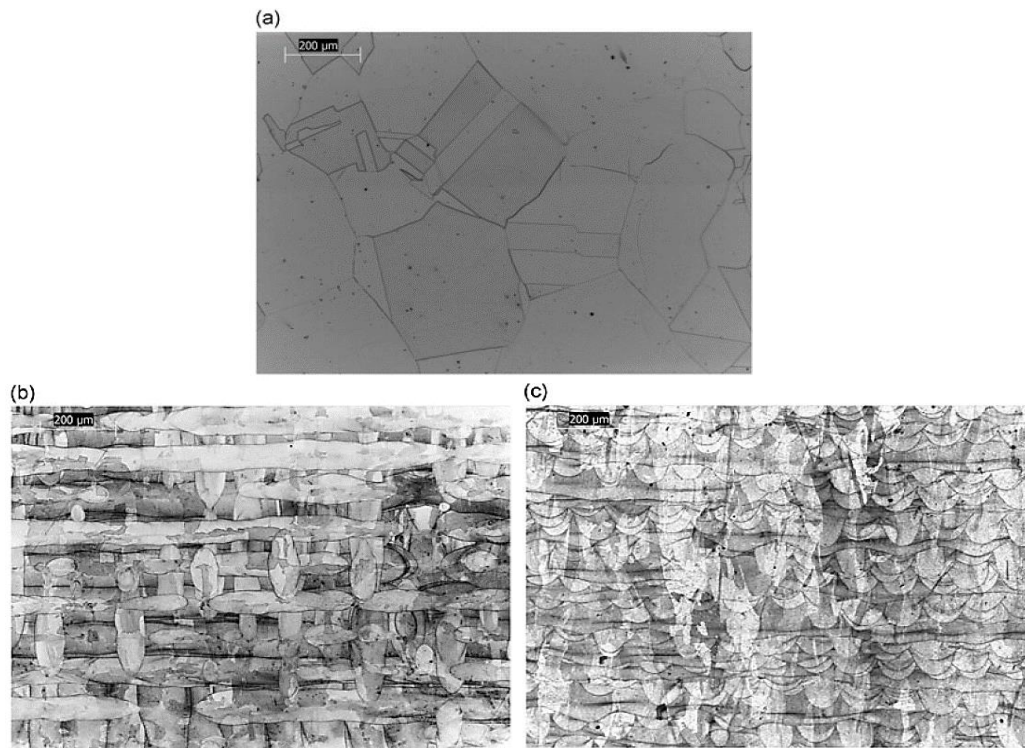


Figure 6 The microstructures of different samples, (a)-wrought, (b)-SLM XY 316 L stainless steel, and (c)- SLM XZ 316 L stainless steel [40]

Figure 6 shows the difference between the microstructures of a wrought 316L sample and an SLMed 316L sample. When compared to the wrought samples, SLMed stainless steel did not have MnS inclusions, which were thought to be sensitive to pitting corrosion [40]. Whereas, it was

found that the main cause of pitting corrosion in SLMed 316L stainless steel was that it had pores [41]. Based on previous studies [42], the shapes of some pores were looked at before and after the CPDP testing.

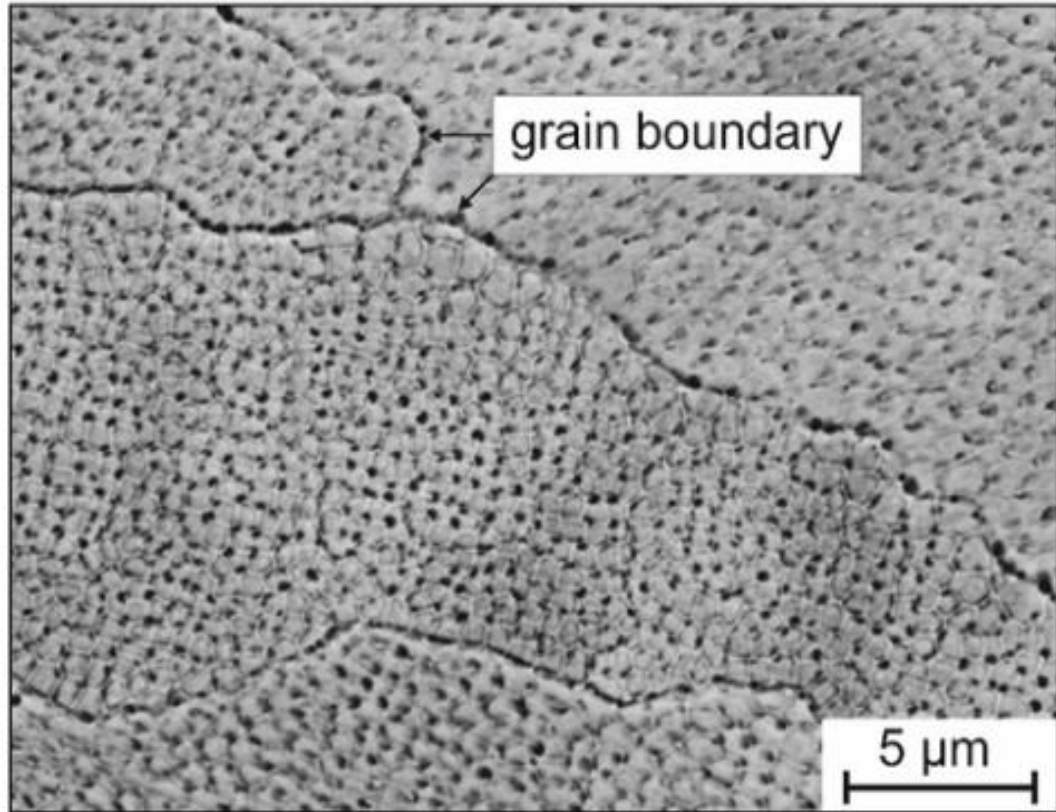


Figure 7: Substructure of SLMed 316L is composed of coarse grains with a cellular substructure. [43]

Figure 7 shows the Substructure of SLMed 316L is composed of coarse grains with a cellular substructure. The structure of columnar and cellular grain or subgrain best describes the SLMed 316L stainless steel microstructure at a micro-scale. A highly fine microstructure is created by the borders of the cellular and columnar subgrains. The breadth of the columnar subgrains is comparable in size to the cellular subgrains, which are typically less than 1 μm [43].

2.6 Effect of The Heat Treatment on Microstructure and Corrosion Behavior of SLMed 316L Stainless Steel

Using the cyclic potentiodynamic polarization (CPDP) technique, Jai Li et al. [44] investigated the electrochemical behavior of 3D-printed 316L stainless steel following heat treatment. The corrosion behavior of 3D-printed 316L stainless steel as deposited (without heat treatment) was compared with the heat treated samples. His study's objective was to investigate the phase transformation behaviors and microstructure evolution of additively manufactured 316L during heat treatment, while optimizing its mechanical and corrosion properties.

Table 1: AM 316L Specimens Heat treatment temperature and time.

No.	Heat treatment
1#	1000 °C/1 h,WQ
2#	1100 °C/1 h,WQ
3#	1200 °C/1 h,WQ
4#	1200 °C/4 h,WQ

Five specimens were used in the study and Table 1 shows that they were heat treated at 1000, 1100, and 1200 °C for one hour before water quenching (WQ). In addition, heat treatment at 1200 °C for four hours and water quenching create a fully austenitic microstructure. The fifth sample was not heat treated to be compared to the others.

The δ and σ phases in as-deposited steel have exquisite vermicular morphology within the γ matrix (Figure 8(a)). Steel has no carbide due to its low carbon content [45]. In Table 2, the volume fraction (vol%) of δ and σ phases in as-deposited and heat-treated steels is calculated from SEM images in figure 8. The δ and σ phases have volume fractions of 7.84 and 4.45 vol%, respectively.

Table 2: Volume fraction values of δ and σ phases in as-deposited and heat treated AM 316L (vol%).

	δ	σ
As-deposited	7.84	4.45
1000 °C/1 h,WQ	3.92	6.98
1100 °C/1 h,WQ	5.79	0
1200 °C/1 h,WQ	3.96	0
1200 °C/4 h,WQ	0	0

When heat treated at 1000 °C for one hour (Figure 8 (b)), σ phase forms by the progressive replacement of δ with effectively no change of the original δ phase morphology, but spheroidization of the remaining δ phase. The volume fraction of δ phase decreases from 7.84 vol% to 3.92 vol%, and σ phase increases from 4.45 vol% to 6.98 vol%. When heat treated at 1100 °C and 1200 °C for one hour (Figure 8 (c) and (d)), σ phase completely dissolves in γ matrix. And the δ phase, with granular morphology, decreases from 7.84 vol% to 5.79 vol% (1100 °C/1 h) and 3.96 vol% (1200 °C/1 h), respectively. When heat treated at 1200 °C for four hours (Figure 8(e)), σ and δ phases completely dissolve in γ matrix with full austenitic microstructure.

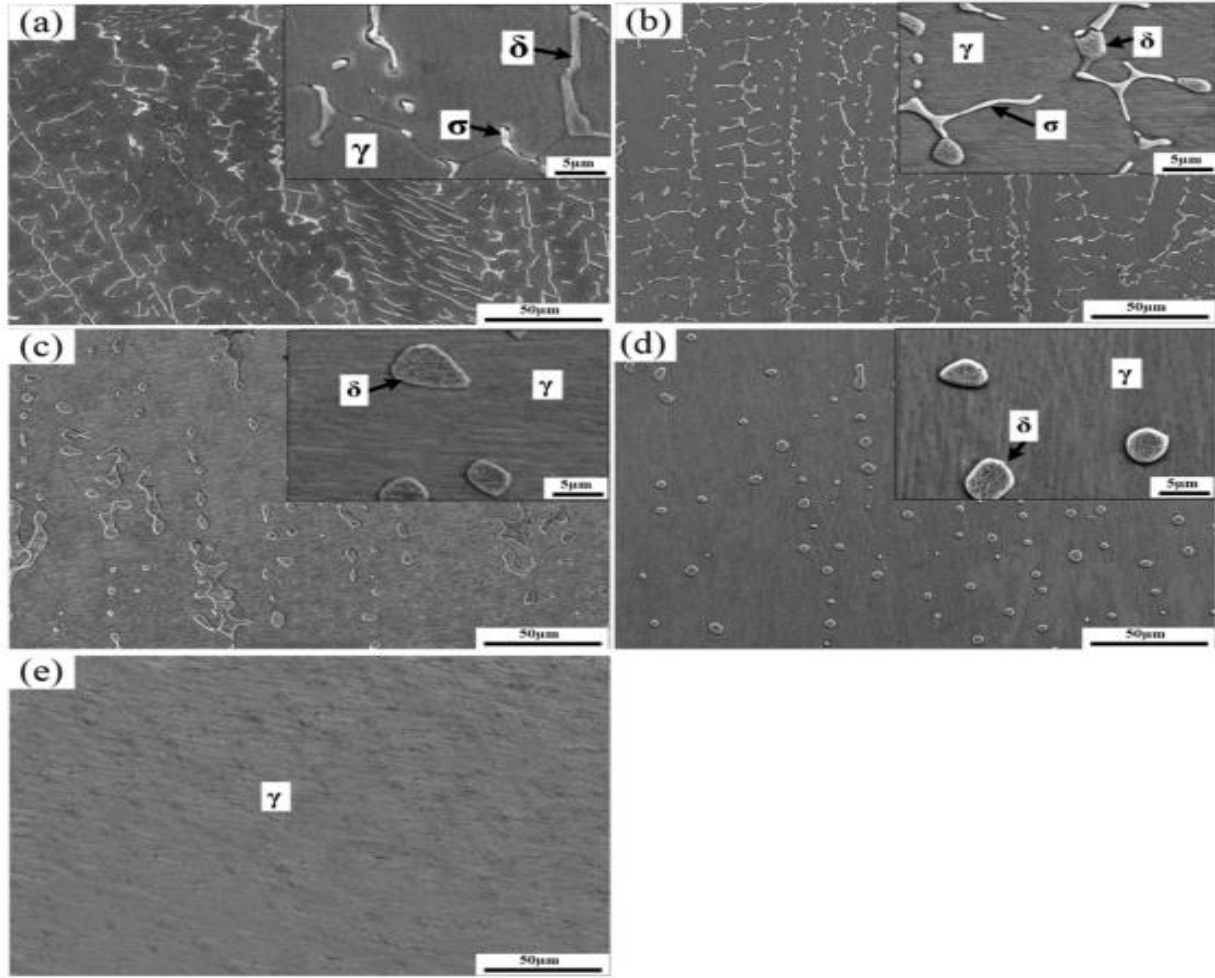


Figure 8: Microstructures of as-deposited and heat treated GMA-AM 316L: (a) as-deposited (b)1000 °C/1 h, (c) 1100 °C/1 h, (d) 1200 °C/1 h, (e) 1200 °C/4 h.

The corrosion properties of as-deposited and heat treated steels in a 3.5% NaCl solution are evaluated using a CPDP method. Figure 9 and table 3 show the corresponding polarization curves and the measured values of the electrochemical parameters. The low corrosion current density (i_{corr}) and high difference between pitting potential and corrosion potential (ΔE) indicate a slow corrosion rate with high corrosion resistance [46], [47]. According to Figure 9 and table 3, the low-

to-high order of i_{corr} is (1200 °C/4 h) < (1200 °C/ 1 h) < (1100 °C/1 h) < (1000 °C/1 h) < as-deposited state as well as the high-to-low order of ΔE . It indicates high-to-low order of corrosion resistance of the steel. The results show that heat treatment can improve the corrosion resistance of steel. Especially, the heat treated (1200 °C/4 h) steel has the best corrosion resistance.

Table 3: Electrochemical parameters of as-deposited and heat treated GMA-AM 316L in 3.5%NaCl

	$i_{corr} / (10^{-8} \text{ A/cm}^2)$	E_{corr}/V_{SCE}	E_p /V_{SCE}	$\Delta E = E_p - E_{corr}/V_{SCE}$
As-deposited	7.83	- 0.15	0.47	0.62
1000 °C/1 h,WQ	6.98	- 0.15	0.57	0.72
1100 °C/1 h,WQ	5.31	- 0.14	0.97	1.11
1200 °C/1 h,WQ	4.68	- 0.16	1.02	1.18
1200 °C/4 h,WQ	4.45	- 0.15	1.10	1.25

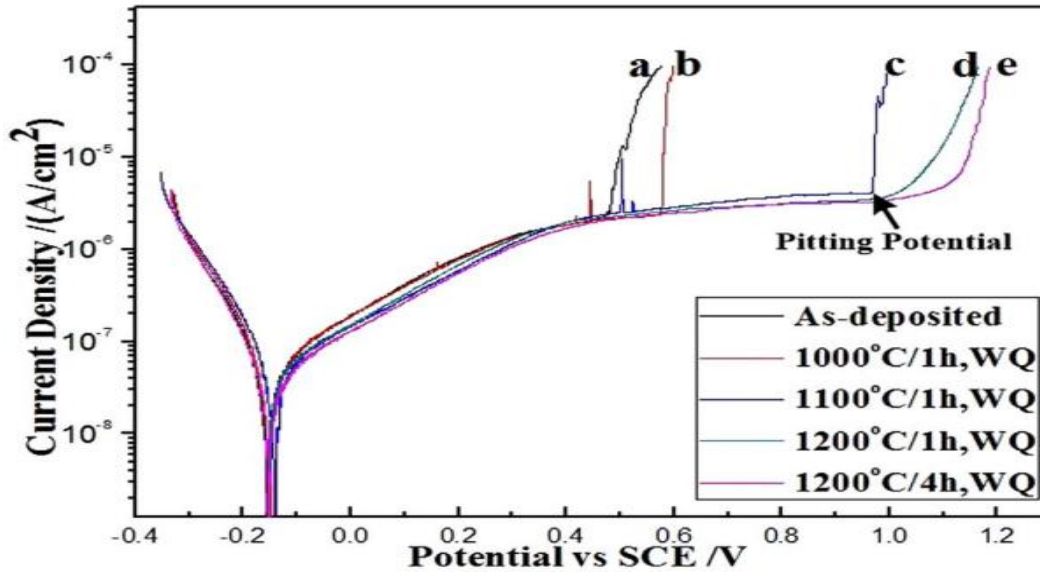


Figure 9: Potentiodynamic curves of as-deposited and heat treated AM 316L in 3.5% NaCl solution at 25 °C:

(a) as-deposited, (b) 1000 °C/1 h, (c) 1100 °C/1 h, (d) 1200 °C/1 h, (e) 1200 °C/4 h.

Finally, the heat treatment has a positive impact on the material properties and enhance a corrosion resistance. The heat treatment improves corrosion resistance of steel, and the corrosion resistance increases with the increase of heat treatment temperature and time. The heat treated (1200 °C/4 h) with full austenitic microstructure exhibits the best corrosion resistance.

2.7 Corrosion of SLMed 316L Stainless Steel

Andreatta et al. [48] studied the electrochemical behavior of a SLMed AISI 316L stainless steel using the cyclic potentiodynamic polarization (CPDP) technique. The corrosion behavior was compared with wrought 316L stainless steel samples having similar composition using NaCl solution (3.5 wt.%) with two different pH values (1.8, 7). It was found that the oxide film is significantly more protective on SLM specimens than on their wrought counterparts in a neutral and acid (pH 1.8) 3.5 wt% NaCl solution. In other words, the SLMed sample illustrate a higher potential in CPDP curve than the potential observed in the wrought 316L sample which mean that the passivity layer of the SLM sample is thicker than the passivity layer wrought sample.

Another study [49] reported similar results when comparing the pitting corrosion of wrought and SLMed 316L stainless steel samples in 0.6 M NaCl solution using cyclic potentiodynamic polarization (CPDP). It was found that the 3D printed sample has a better pitting corrosion resistance compered to wrought sample. This behavior may be due to the removal/refinement of MnS inclusions in the SLM-produced specimen, which have previously been identified as preferred locations for pit start in commercial 316L stainless steel.

A follow-up study [50] was also conducted to determine the underlying mechanism of pitting

corrosion induced by pores via the investigation of pit growth and passivation procedure. Several NaCl solutions with pH values ranging from 1 to 13 (odd numbers) and a 6% FeCl₃ solution were selected for pitting potentials using the CPDP technique. The SLMed 316L samples were highly sensitive to pitting in solutions with low pH values (1 and 3). Whereas, wrought samples were more prone to pitting corrosion in the rest of the solutions. A morphological analysis of both samples indicated that metastable pits are abundantly available in wrought samples. In SLM samples, however, such pits rapidly transformed into stable growth.

Woźniak, et al. [51] performed pitting corrosion tests on 316L stainless steel samples using the PDP method (figure 10). The corrosion performance using a Ringer's solution was studied as a function of energy density ranging from 100 to 1333 mJ/mm³ and other variables by forming different groups of samples. It was found that samples fabricated using a laser energy density of 600 mJ/mm³ exhibited the most optimal characteristics such as mean density closer to 98% and a fully homogenous γ austenite microstructure without defects. Generally, the polarization curves exhibited similar characteristics for all tested samples. However, the best-performing samples possessed optimal resistance to corrosion with a mean corrosion potential of -133 ± 5 mV.

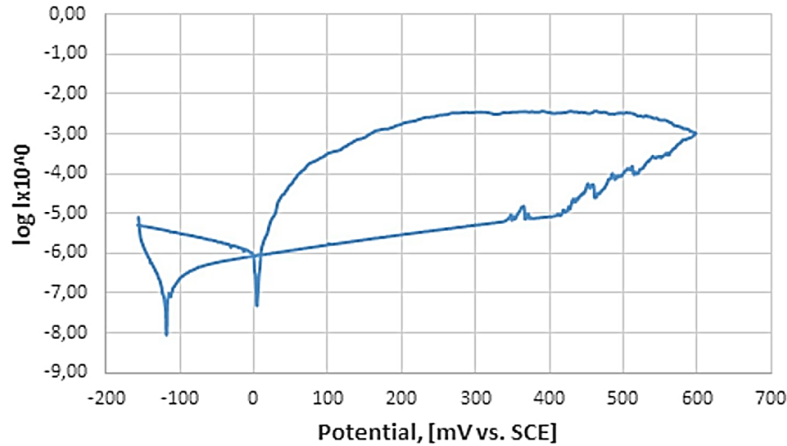


Figure 10 Polarization curves for the best-performing samples. [51]

This concept was further studied by Maicas-Esteve, et al. [52] via a design of experiments (DoE) using ANOVA to delineate the relationship between several SLM parameters such as scanning speed and laser energy density (ranging from 51.17 to 173.91 J/mm³). The primary objective of the study was to reach an optimum combination of process parameters enabling the lowest porosity and highest resistance to pitting corrosion in acidic environments (e.g., 3.5 wt. % NaCl). The statistical analysis using ANOVA revealed that laser scanning speed had maximum influence (~75%) on the porosity distribution followed by fabrication axis (~29%) and energy density (2.3%). The CPDP results (shown in the figure 11) revealed that repassivation and positive breakdown potentials were maximum in SLM samples having porosity <1. Like previous studies, no MnS inclusions were found in 316L stainless steel samples and the presence of pores was found to be the main reason for the pitting corrosion.

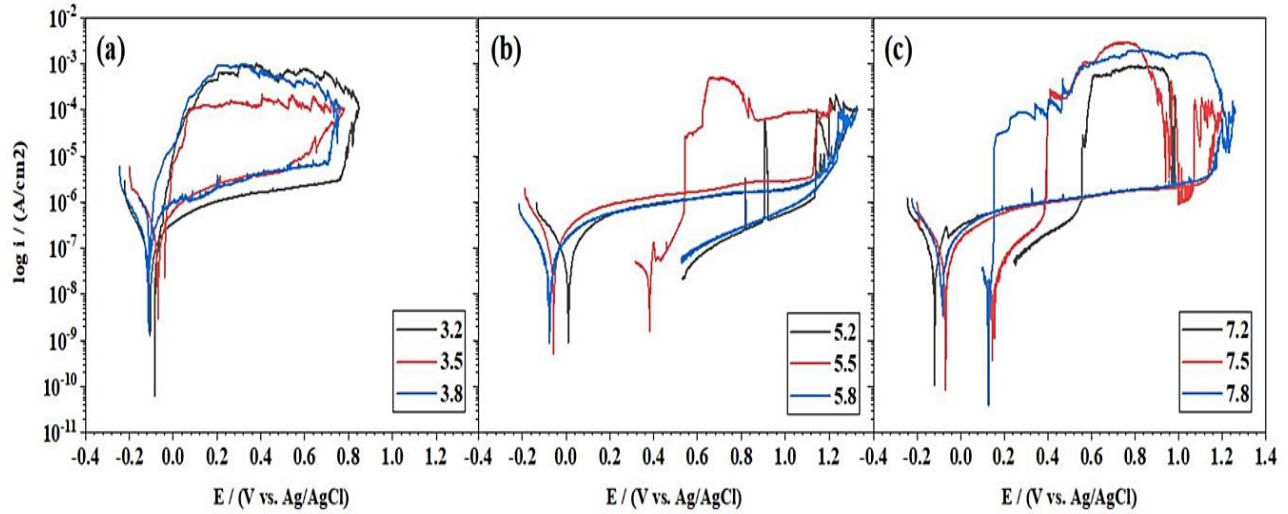


Figure 11 CPDP curves at positions 2, 5, 8 with different energy densities (a) 52.17 J/mm³, (b) 89.44 J/mm³, (c) 173.91 J/mm³ [52]

An analysis of existing literature signifies the fact that the corrosion behavior of SLMed 316L stainless steel is largely determined by the microstructure that results from the production or post-processing procedures. Therefore, it is vital to understand how the expected and non-expected characteristics of the SLMed 316L stainless steel, such as surface finish, the percentage of inclusions, microstructure, and porosity level, affect its corrosion performance.

The porosity does not significantly impact the breakdown of passivity (E_{pit}) in potentiodynamic polarization curves for materials with holes larger than 10 μm but it does affect metastable pitting and SLMed 316L stainless steel repassivation [42]. The pitting potential was only slightly changed by scan speed, although materials obtained with scan speeds between 1,000 and 1,400 mm/s had a larger density of pits due to pores of increasing size and number [34].

In recent years, a subject of growing attention is the relationship between the intricate

microstructure of SLMed 316L stainless steel and its corrosion behavior. There is still a significant deficit in the current literature regarding the correlation between the AM process parameters and the corrosion properties of the AMed alloys. Furthermore, the underlying mechanism behind the dissolution of these alloys has yet to be fully comprehended.

For example, table 4 highlights the literature results regarding the corrosion resistance of SLMed 316 L stainless steel in various electrolytes. Some studies indicated a better performance compared to the conventional counterpart, while others suggest otherwise. The SLMed 316L stainless steel is frequently considered more corrosion-resistant than a standard wrought stainless steel having the same composition [42]. In some situations, a complex microstructure and the existence of flaws impart inferior corrosion resistance to its wrought counterpart [53].

Table 4: Summary of previous studies concerning the microstructural and corrosion of SLMed and wrought 316L stainless steel.

Target Material	Electrolyte	Laser power (W)	Hatch distance (μm)	Layer thickness (μm)	Scan speed (mm/s)	Energy Densities (J/mm^3)	Key findings	Ref.
SLMed 316L	Simulated body fluid	≤ 220	25	25	-	-	SLMed 316L at high laser power shows better corrosion resistance	[54]
SLMed 316L	Dilute sulfuric acid	200	100	30	-	-	Electrochemical corrosion > commercial wrought	[55]
SLMed 316L	NaCl (0.6 M)	150	80	30	600	104	Erosion-corrosion resistance < commercial counterpart	[49]
SLMed 316L	NaCl (0.1 M)	90	105	30	1000	29	Electrochemical corrosion > commercial counterpart	[56]
SLMed 316L & SPS 316 L	NaCl (3 wt.%)	200	100	30	800	83	Electrochemical corrosion > Spart plasma sintered & as-rolled counterparts	[57]
SLMed 316L	-	80-480	100-30	-	493-2958	1.3 to 46.7	Properties of SLMed samples directly depend on SLM parameters	[58]
SLMed 316L	3.5wt.% NaCl, and 20% H ₂ SO ₄	400	110	30	230	527	Uniform corrosion in H ₂ SO ₄ and more resistance than NaCl	[59]
SLMed 316L	-	100	100	60	90 - 180	-	Higher scan speed decreased molten pool size	[10]
SLMed 316L	-	100	-	30 -150	400 - 600	-	The mechanical properties depend on many factors.	[60]
SLMed 316L	-	160 - 190	-	30 - 60	800 - 1200	-	variation in the measured density, tensile strength performance and in micro-	[61]

							structure	
SLMed 316L	0.6 M NaCl solution	150	80	30	600	-	pitting corrosion resistance of the SLM- 316L better than wrought	[62]
SLMed 316L	3.5 wt. % NaCl solution	80 - 240	110	50	750	-	new type of pitting was found in 3-D printing	[63]

As evident from the above table , the selection of process parameters is highly sensitive in regulating the corrosion behavior, microstructure, and mechanical characteristics of the SLMed 316L stainless steel. The microstructure and characteristics of these materials can also be significantly altered by heat treatment [64]. The SLM technique modifies inclusions in 316L stainless steel that are responsible for controlling corrosion. Whereas, the stainless steel inclusions have not been linked to any localized attacks. It is often proposed that SLM-based fabrication may limit the production of inclusions during the melt pool's fast solidification. Likewise, it may lead to the generation of nanoscale inclusions that are insignificant in size for localized corrosion [42], [65].

The SLMed 316L stainless steel often differs from conventionally produced 316L stainless steel in several ways such as anisotropic grain shape and uneven microstructure for example. Sensitization, which can result in continuous corrosion along grain boundaries in 316L stainless steel, can be found in SLMed materials [66]. Additionally, preferential stress corrosion cracking in the build direction can also take place [35].

However, the causes of corrosion in SLMed stainless steel under a marine-like environment are

still poorly understood [67]. A significant number of studies have previously investigated the impact of marine settings on stainless steel materials. Most of them have reported the relationship between printing settings and resulting microstructures. However, the corrosion behaviors of stainless steel materials in specific corrosive environments have yet to be investigated.

In the study by Bang et al. [58], the impact of various SLM process conditions on the fabrication of 316L parts was explored, and analyzed the corresponding changes in characteristics. The primary aim was to study the impact of energy density on 316L by examining the interaction of microstructure, mechanical property, and chemical composition. A series of experiments using 36 different process conditions and the microstructure of complete melting energy specimens are shown in figure 12 with marked blue line. The SLM machine processed the energy density map in the figure 13, and the yellow dotted line corresponded to the theoretically calculated energy density while the fabricated specimens marked with black circles. The findings indicate that as energy density increased, the strength and elongation of the parts decreased rapidly. However, an increase in hardness was also observed, and this phenomenon was due to an increase in brittleness caused by the high oxygen content. The hardness improved as the energy density increased, but the brittleness also increased due to the higher oxygen content. This led to a conclusion that there is a need to extend analysis at low energy densities to explore the SLMed and wrought stainless steel corrosion behavior in acidic solutions with different pH.

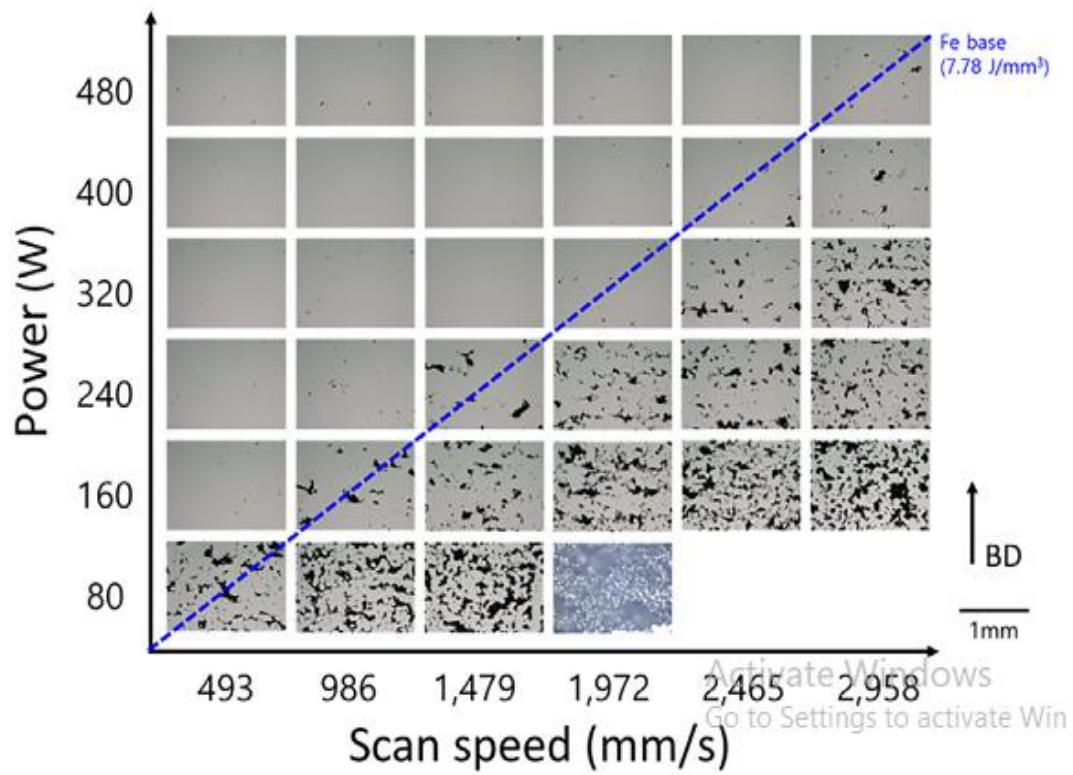


Figure 12: Microstructure image of 316L SLMed specimens with blue line dot for almost complete melting energy density

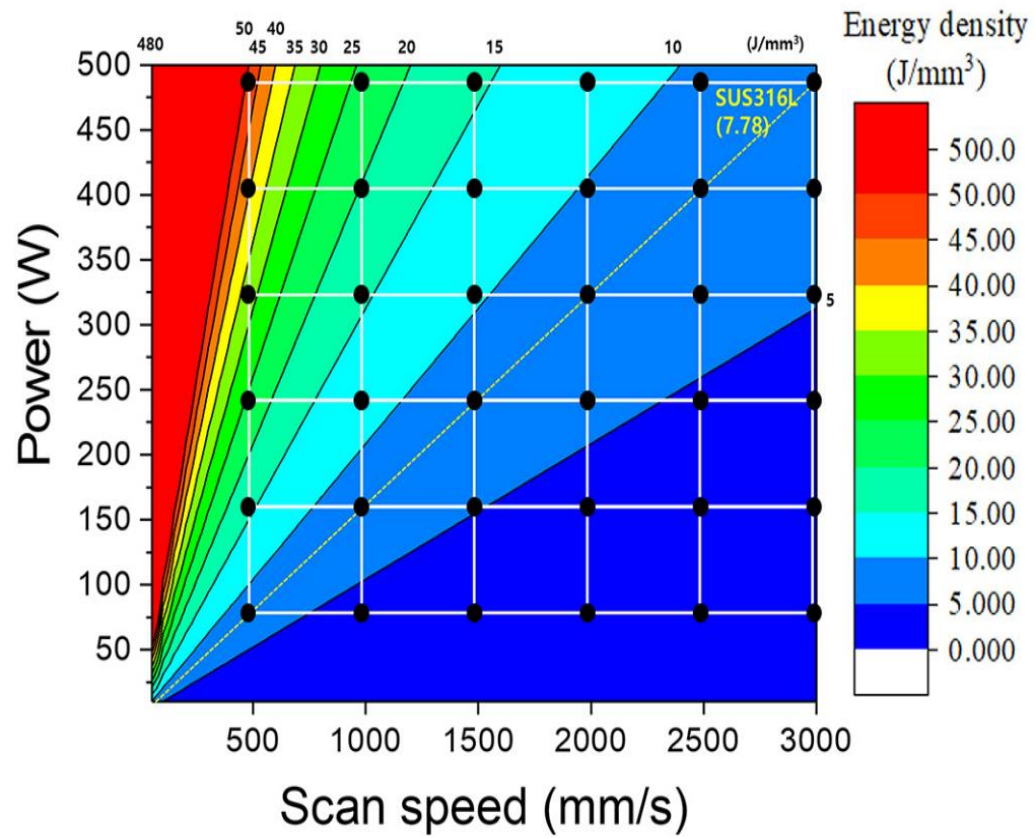


Figure 13 SLM process conditions Map with the theoretically calculated melting energy density. [58]

CHAPTER 3 AIM OF THE RESEARCH

3.1 Research Motivation

It is important to mention that most of the conducted studies for 316L were focused on one parameter of the SLM process, either laser power or scan speed. However, it is very important to pay attention to the energy density of SLM and the other process parameters. This was also highlighted by Maicas-Esteve [52], who suggested that the microstructure variation should be connected and linked to the energy density of the SLMed sample instead of the individual parameters of the SLM process like laser power or scan speed. In addition to that, it was observed from the literature review (Section 2.5 and section 2.6) that there hasn't been any published research on the impact of porosity and low energy density on the corrosion of 316L stainless steel produced by AM in a hydrocarbon environment.

Therefore, it is crucial to conduct further research on the effects of porosity and input energy density on the corrosion behavior of 316L stainless steel produced by AM/SLM in a hydrocarbon environment, as this can have significant implications for its practical applications in industries such as oil and gas. This research could potentially lead to the development of more corrosion-resistant materials and improve the overall reliability and safety of equipment used in these industries.

3.2 Research Objectives

The primary focus of this research was to study the microstructure and corrosion behavior of 316L stainless steel fabricated using SLM with different energy densities in 3.5% NaCl solution with different pH values as well as hydrocarbon (crude oil) environment. The corrosion behavior was compared to that of wrought 316L stainless steel. The specific objects were:

- Study the effect of input energy density variation on corrosion behavior of 3D printed 316L stainless steel immersed in 3.5 wt. % NaCl solution at room temperature.
- Study the effect of pH variation on corrosion behavior of 3D printed 316L stainless steel immersed in 3.5 wt. % NaCl solution at room temperature.
- Study the corrosion behavior of the optimum sample of 3D printed 316L stainless steel immersed in Hydrocarbon environment (Crude oil that used in oil and gas industries) at room temperature and pH 1 and compare with 3.5% NaCl at pH1.
- Study the effect of high temperature (70 °C) on the corrosion behavior of the optimum sample of 3D printed 316L stainless steel immersed in 3.5 wt % sodium chloride solution at pH 1 (simulation for brine water temperature in the crude unit in the refinery).

CHAPTER 4 EXPERIMENTAL PROCEDURE

In this chapter, explanation how the experiments were done and what methods were used to reach the main objective of the study. The methodology sections will provide a detailed explanation of the research materials, fabrication methods, density measurement, microstructure characterization, electrochemical corrosion test and immersion corrosion test. Figure 14 shows the flow chart of the experimental procedure for each section that was followed in this study, which also includes the section numbers for more details.

4.1 Materials

The 316L stainless steel has been selected for this work due to its important in oil and gas industry and less available research in industry environment. The chemical composition of SLMed and wrought samples that used in this study is shown in table 5.

Table 5:Chemical composition (in wt.%) of wrought and 3D printed 316L stainless steel.

Elements	C	Mn	Mo	S	P	O	Ni	Cr	Fe
SLMed	0.03	2	2.25	0.01	0.025	0.05	13	17.1	Bal.
Wrought	0.03	2.2	2.3	0.03	0.05	0.05	11.2	17.5	Bal.

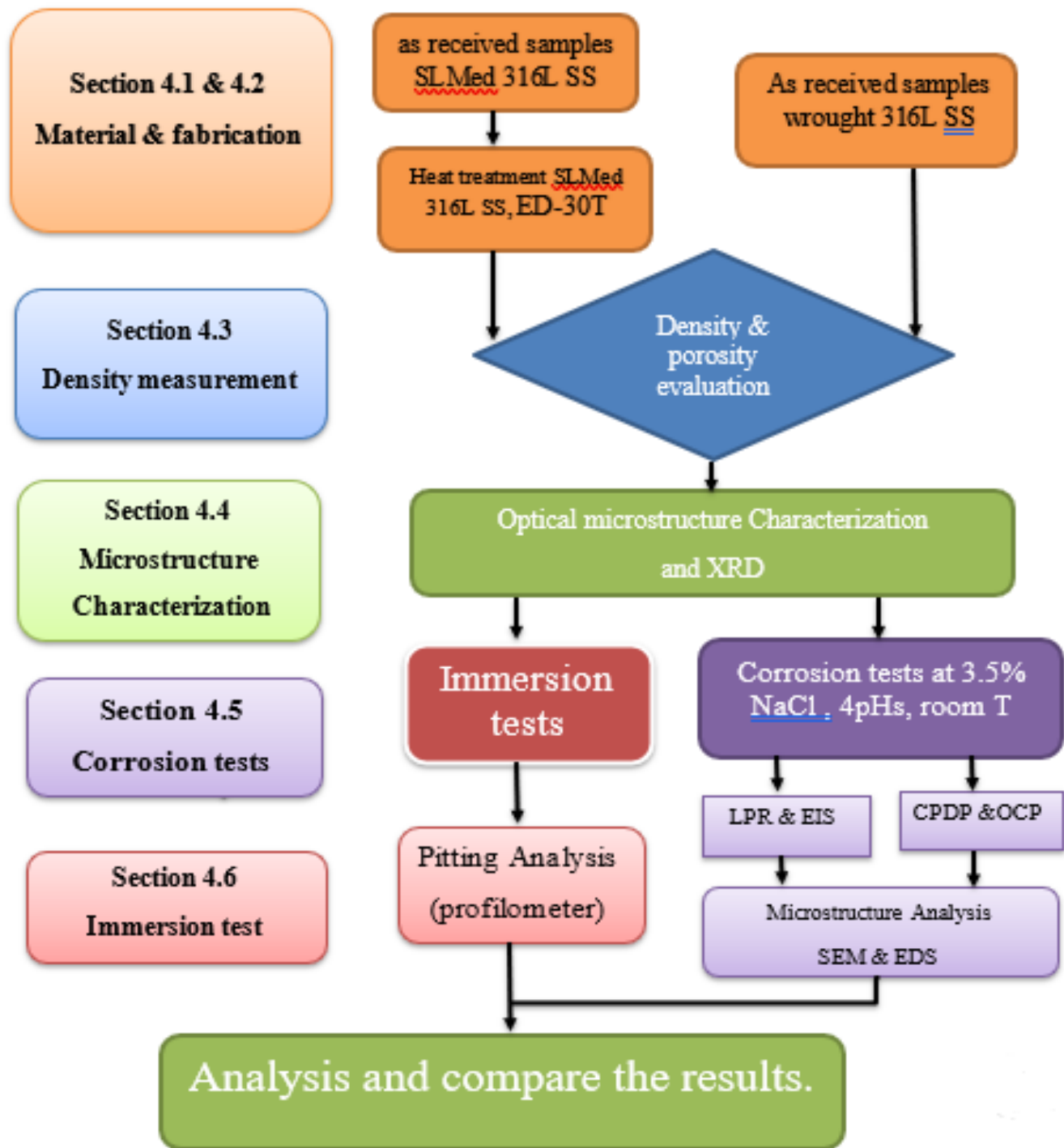


Figure 14: Flow chart of experimental procedure

4.2 Fabrication

The wrought samples was fabricated by using conventional casting methos and were bought from the local market. The SLMed 316L stainless steel samples were fabricated by using Selective Laser Melting (SLM). The samples were printed with different energy densities, as calculated by the formula below:

$$E_d = \frac{P_{laser}}{v_{scan} S_{hatch} t_{layer}} \quad (4.1)$$

Table 6 shows SLM process parameters of 3D printed 316L. The calculated energy densities were 21 J/mm³ (ED20), 33 J/mm³ (ED30), and 41 J/mm³ (ED40). These samples were tested in their original state, without any heat treatments to relieve stress or change the way the crystals form. The ED30T sample was heat treated at 550 °C for 2 hours before being cooled by air. Figure 15 shows as built sample of ED-30 3D printed during the SLM process.

Table 6: SLM process parameters of 3D 316L printed and wrought 316L stainless steel samples.

Sample Name	Laser power (W)	Scan speed (mm/s)	Layer thickness (mm)	Trace width (mm)	Energy density (J/mm³)
ED20	180	1270	0.045	0.15	21.0
ED30	180	800	0.045	0.15	33.3
ED30T	180	800	0.045	0.15	33.3
ED40	180	650	0.045	0.15	41.0
W-316L	conventional manufacturing for 316L stainless steel - Wrought Sample of 316L				
Note: - ED20, ED30 and ED40 are as received from the SLM machine without any stress relief. - ED30T is ED30 sample with stress relief.					

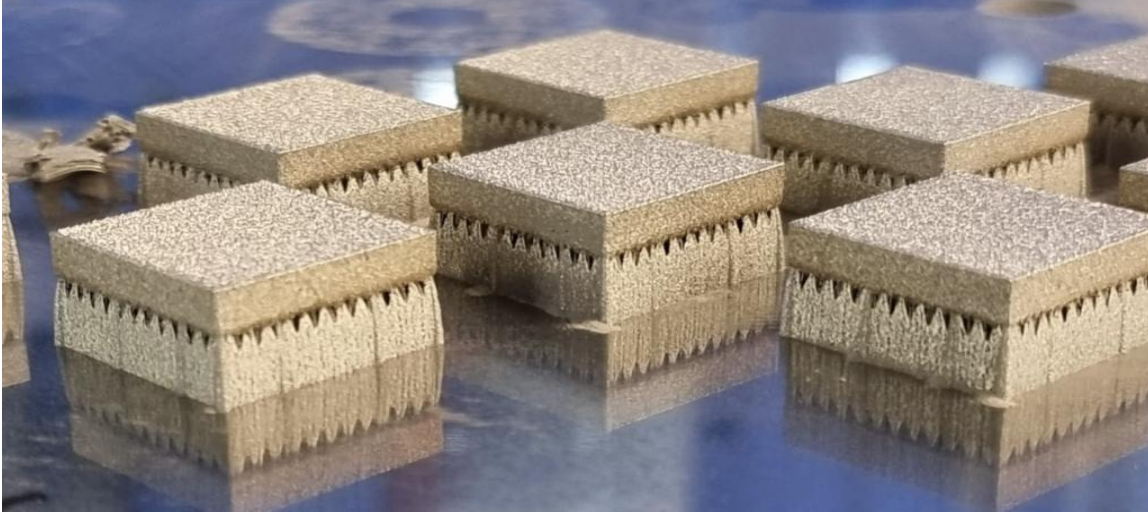


Figure 15: the fabricated sample of ED-30 3D printed by SLM

4.3 Density Measurement

The relative density of wrought 316L stainless steel and all SLMed 316L stainless steel specimens were measured according to the Archimedes technique. Both samples weight were measured in air and distilled water. The below equation was used to calculate the experiment density.

$$\rho = \left(\frac{A}{A-B}\right)(\rho_o - \rho_a) + \rho_a \quad (4.2)$$

Where ρ is density of sintered sample (Experimental density) in g/cm³, A is weight of sintered sample in air, B is weight of sintered sample in distilled water, ρ_o is density of distilled water, ρ_a is density of air. The relative density present was calculated by use the below equation and use the theoretical density of the stainless steel which is 7.93 g/cm³

$$Relative\ density\ (\%) = \frac{Experimental\ density}{Theoretical\ density} \quad (4.3)$$

4.4 Microstructure Characterizations

The sample surfaces were prepared according to the standard metallography sample preparation [68]. The samples were cut using a circular saw to display the material's side view. The sample surfaces were ground using silicon carbide grinding paper having grit sizes 120, 240, 400, 600, and 800 respectively followed by polishing using 0.1 μ aluminum oxide suspension liquid. The samples were then cleaned with water, washed with ethanol, and dried with warm air. To reveal the microstructure of samples, a solution having 3 parts nitric; 1-part HCL; 5 parts deionized water was used as an etchant.

Etched samples of wrought 316L stainless steel and SLMed 316L stainless steel were characterized using Optical Microscope (GX53 olympus) to obtain and evaluate the microstructure of all samples before corrosion test. Also, XRD was performed to analyze the characterizing crystalline materials and obtain more information about the structure, phases and crystallinity. The diffractometer (XRD, Rigaku MiniFlex, Japan) was operated with Cu K α 1 at a 0.15416 nm wavelength, 10 mA current, and 30 kV voltage to study the structural changes. After corrosion tests, Scanning electron microscopy (SEM) with an accelerating voltage of up to 20 kV coupled with an energy-dispersive X-ray spectroscopy (EDX) silicon drift detector were used to evaluate the corrosion behavior, the microstructural development resulting from various pH values and elemental analysis of SLMed and wrought samples.

4.5 Electrochemical Corrosion Test

Electrochemical corrosion measurements were conducted to reveal the corrosion behavior and the effect of fabrication of the SLMed samples with different energy densities. The corrosion tests

were done using a potentiostat (Reference 3000, Gamry Instruments, USA) with a three-electrode cell: the reference electrode, the working electrode, and the counter electrode. These electrodes are saturated calomel electrode (SCE) type. The Open Circuit Potential (OCP) was held for 1 hour so the electrolytic system could attain equilibrium. All electrochemical experiments were conducted in 3.5% NaCl at room temperature with four pH values; pH-1, pH-3, pH5, and pH 7.5. The pH values were controlled by adding HCl to the solution.

The Linear Polarization Resistance (LPR) was measured between -25 and +25 mV against OCP at 0.125 mV/s. from Stern-Geary Equation, I_{corr} was calculated and use the below equation to calculate the corrosion rate in mpy

$$Corrosion\ Rate\ (mpy) = 0.13\ I_{corr}\ \frac{(EW)}{d} \quad (4.4)$$

Where I_{corr} is corrosion current, amperes or Amperes/cm²., EW is is the equivalent weight, d is the density in g/cm³, mpy is milli-inches per year. The Stern-Geary Equation is shown below where R_p is slope at the origin of the polarization resistance plot in ohms, β_a and β_c are tafel constants from a tafel curve, volts/decade of current.

$$I_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a \beta_c)} \quad (4.5)$$

The Cyclic Potential Dynamic Polarization (CPDP) test was performed to evaluate the pitting corrosion of 316L SLMed samples and 316L wrought samples and study their susceptibility to localized corrosion. It was performed at a scan rate of 1 mV/s and 0.5 V away from the OCP.

Using the Tafel technique, the anodic and cathodic curves were extrapolated to produce E_{corr} and i_{corr} .

Electrochemical impedance spectroscopy (EIS) measurements were done from 100 MHz to 100 kHz with 10 points per decade at OCP. All corrosion experiments employed a 1 cm² open-air sample. The fitting and analysis of electrochemical data were carried. Figure 16 shows the electrochemical test set up for the room temperatures.



Figure 16: electrochemical test set up for the room temperatures.

4.6 Immersion Corrosion Test

The heat treated 316L SLMed (ED30T) stainless steel and the 316L wrought samples were immersion in 3.5% NaCl and crude oil (hydrocarbon) for 14 days at room temperature. Figure 17 shows the solution preparation for the immersion test for both crude oil and 3.5% NaCl solution. The pH was controlled by adding HCl drops in 3.5% NaCl and crude oil until the pH reduced to be pH 1. Samples weight were measured before immersion them in the solutions. After immersion test, for 14 days, the samples were cleaned and their weight measured as per ASME standard G31 Standard Guide for Laboratory Immersion Corrosion Testing of Metals and G1-Preparing Cleaning and Evaluating Corrosion Test Specimens [68], [69]. The weight of each specimen was measured five times before and after the immersion test. The corrosion rate in mpy was calculated by equation 4.6:

$$CR = \frac{(3.45 \times 10^6) * W}{A * T * D} \quad (4.6)$$

where:

CR = corrosion rate in mpy

T = time of exposure in hours,

A = exposed surface area in cm² to the nearest 0.01 cm²

W = mass loss in g

D = density in g/cm³.

As per ASTM standard G46 [70], an optical profilometer was used to measure and evaluate the pitting corrosion of the samples that were immersed. Each sample was scanned in at least three spots, everyone with area of 5 mm². The pit density, maximum pit depth, average pit depth and

pit size were evaluated for each sample. The number of visible pits over an area of 5 mm² is used to figure out the density of pits. The pit depth is demonstrated in both maximum pit depth and average pit depth with the mean of a minimum of five deepest pits. For high temperature test, the 3.5 % NaCl solution at pH1 was used and the temperature was controlled by using Witeg laboratory hot plate (DH.WHP Series) equipped with a sensor to maintain the test temperature. The test temperature was at 70 C to simulate the brine water temperature at crude unit in the refinery. Figure 18 shows the electrochemical test set up for the high temperature corrosion test.

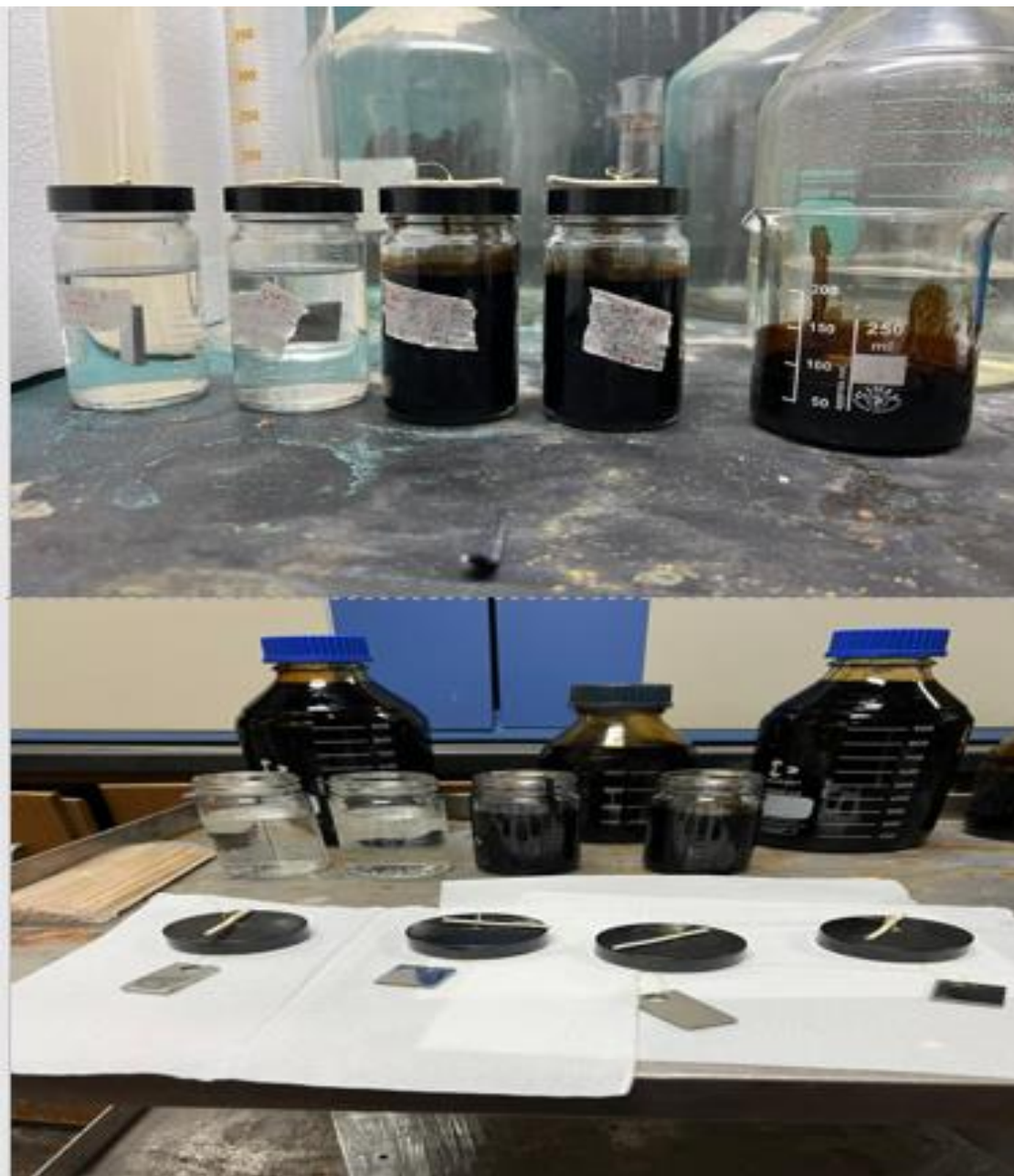


Figure 17: preparation of immersion test for ED-30T and W-316L in NaCl solution and crude oil for 14 days

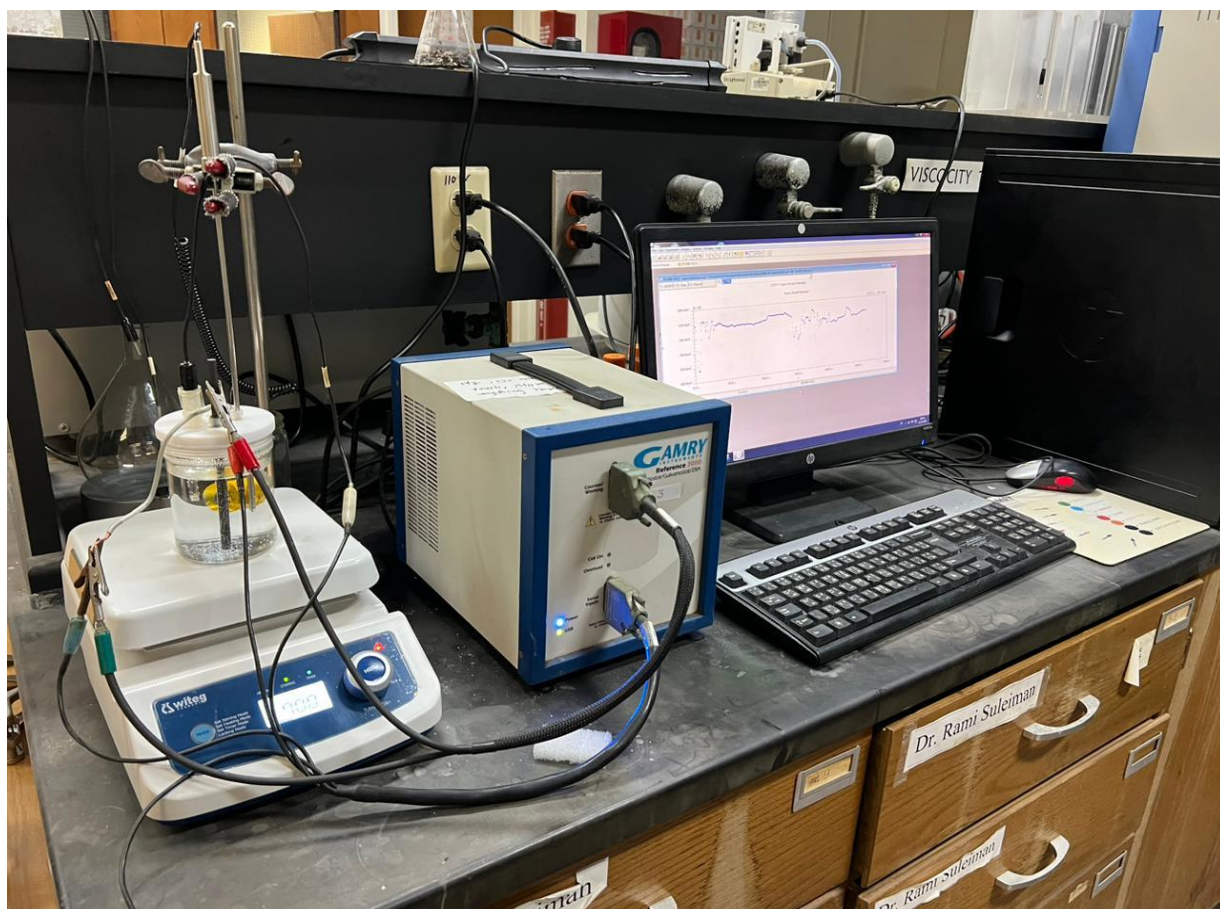


Figure 18: electrochemical test set up for the high temperatures.

CHAPTER 5 RESULTS AND DISCUSSION

5.1 Relative Density and Porosity

Table 7 shows the relative density and porosity of the samples fabricated with different energy densities. ED-30T and W-316L have the lowest porosities of 0.19 % and 0.32 %, respectively. The relative density of 3D samples increases as the energy density increases until it reaches 99.81% at 33.3 J/mm³. However, at 41 J/mm³, this percentage drops to 98.8%. Jiang, et al. [71] reported that some energy densities above 41 J/mm³ have a relative density lower than 98 %. It was reported by Li, et al. [10] that when the scan speed of SLM increases the porosity of fabricated metal will also increase. Therefore, it is important to optimize the energy density and scan speed parameters during the 3D printing process to achieve the desired relative density and minimize porosity in the final product. In this study, the ED-30T sample was found to be the best performing considering its highest relative density and lowest porosity.

Table 7: Relative density and porosity of samples used in this study.

Sample Name	energy density (J/mm ³)	Post treatment	relative density	porosity
ED20	21.0	No	93.96% ± 0.02	6.04%
ED30	33.3	No	99.48% ± 0.11	0.52%
ED40	41.0	No	98.89% ± 0.09	1.11%
ED30T	33.3	Yes	99.81% ± 0.04	0.19%
W-316L	conventional manufacturing for 316L SS - Wrought Sample of 316L	Yes	99.68% ± 0.13	0.32%

5.2 Microstructure Analysis

Figure 19 shows the side view microstructure characteristics of ED-20, ED-30, and ED-40 after etching the specimens as received. Melt pool boundaries were observed in all three 3D-printed samples like what was observed in the previous studies working with 316L 3D-printed specimens [1], [52], [72], [73]. The pores were observed in ED-20 and ED-30, but not in ED-40. The reason for such a difference is the low energy density of ED-20. This results in a higher quantity of unmelted powder particles that cause more porosity. The ED-30 has a higher energy density, which allows for better melting of the powder particles and results in fewer pores.

In contrast, both ED-30 and ED-40 demonstrated the production of a hierarchical microstructure, comprising a high density of melt pools, grains, and sub-grains. It can be concluded that high energy density may produce high relative density and low porosity [10]. Finally, thermal gradient and heat flow caused by the laser power of SLM led to an elongated columnar shape of the grain for all 3D printed samples.

Figure 20 shows the side view microstructure of ED-30T (ED-30 after stresses relief) and a wrought sample of W-316L. Grain boundary shapes of ED-30T is similar to the wrought sample W-316L. This similarity in grain boundary shapes indicates that the stress relief process has improved the microstructure of ED-30T, making it comparable to that of the wrought sample. However, further analysis is needed to determine if other mechanical properties have also been improved. To compare all specimens, 3D topography image after etching was taken and shown in figure 21 in 200 pixels. It was observed that there is a clear different in shape and size of the grain.

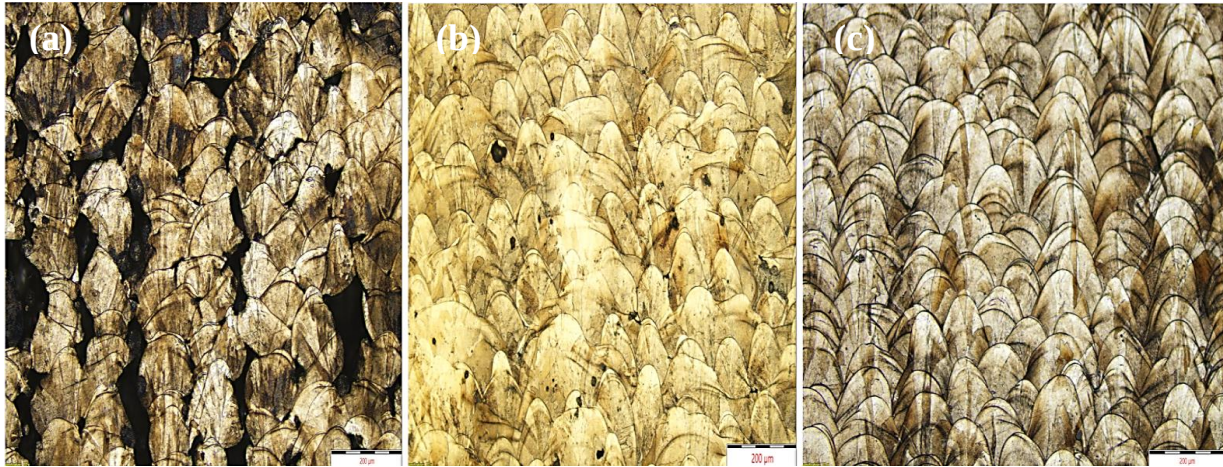


Figure 19 Optical micrographs of as-received (A) SLMed 316L ED:20 (B) SLMed 316L ED:30 (C) SLMed 316L ED:40. 200 Micrometer.

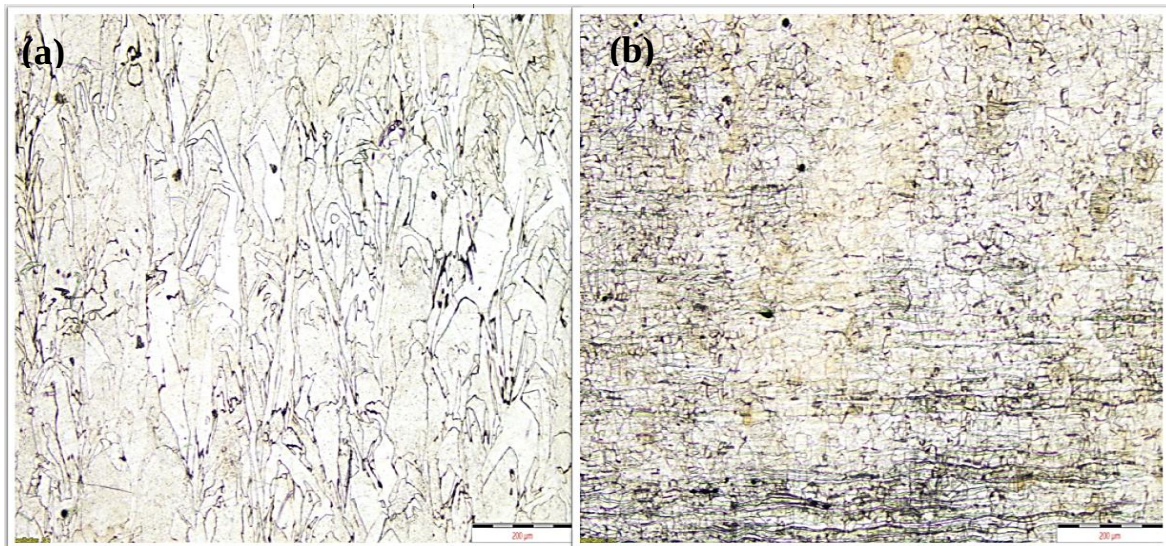


Figure 20 Optical micrographs of (A) SLMed 316L ED:30T with stress relieve (B) as received wrought 316L. 200 Micrometer.

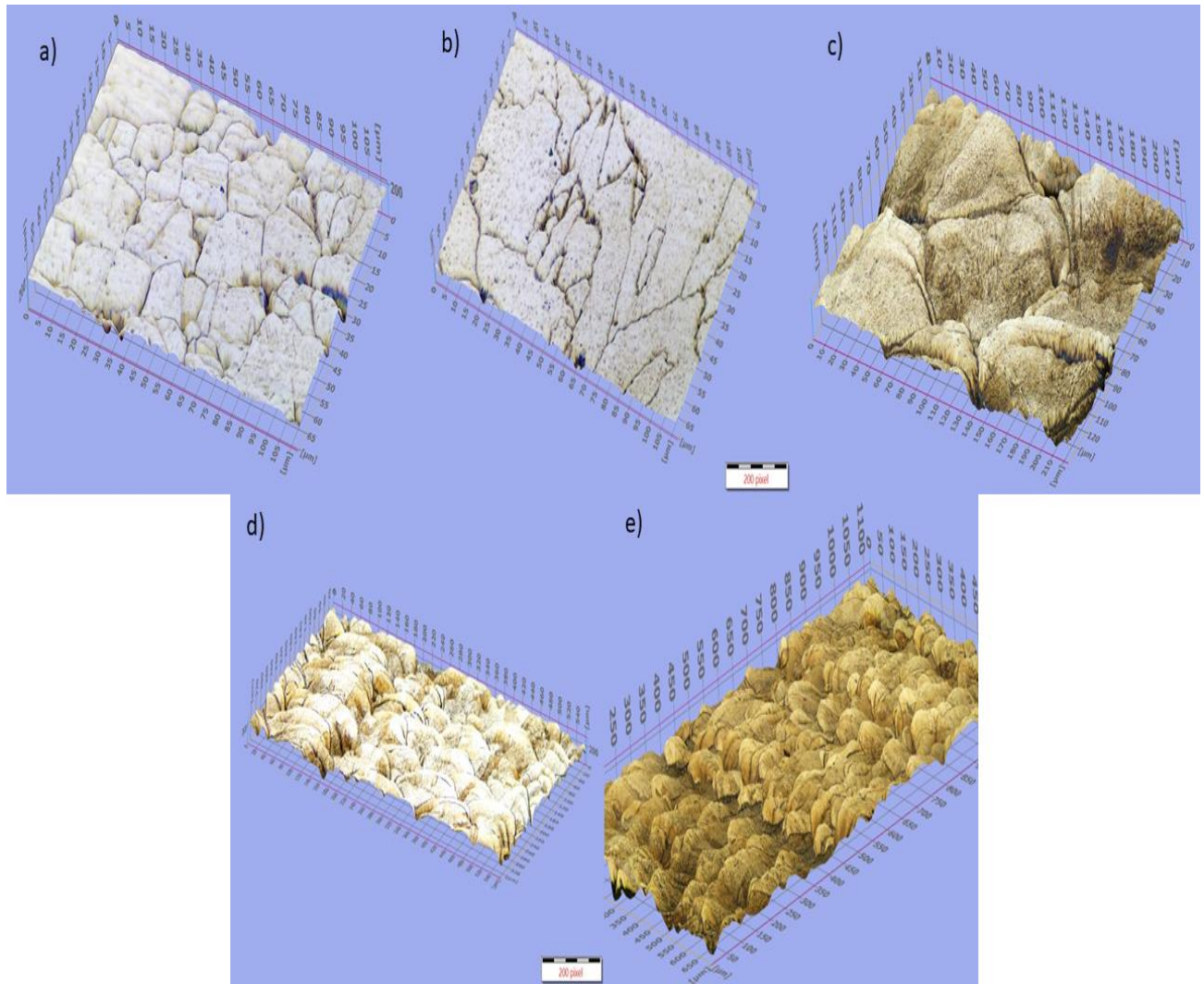


Figure 21: 3D topography image after etching for a) W-316L sample b) ED30T sample c) ED20 sample d) ED30 sample e) ED40 sample.

Figure 22 shows XRD results of the fabricated SLM samples and wrought sample. The SLM 316L had a complete gamma austenite phase but did not contain any martensite phase. Additionally, the SLM samples exhibited a crystal orientation which are indicated as $\gamma(111)$, $\gamma(200)$, $\gamma(220)$ and $\gamma(311)$ crystal planes. It was reported by Xiaoqing Ni et al. [34] that the crystal's axis was perpendicular to the direction that the scanning was done and parallel to the direction that the accumulation layer was built. The laser beam created a temperature differential at the bottom of the elevated molten pool, which was what caused this. This temperature gradient was mostly along the accumulation layer. This phenomenon is known as laser-induced periodic surface structures (LIPSS) and has potential applications in surface engineering, such as creating functional surfaces with controlled wettability or friction. Further research is needed to fully understand the underlying mechanisms and optimize the process parameters for specific applications which is not our focus in this study.

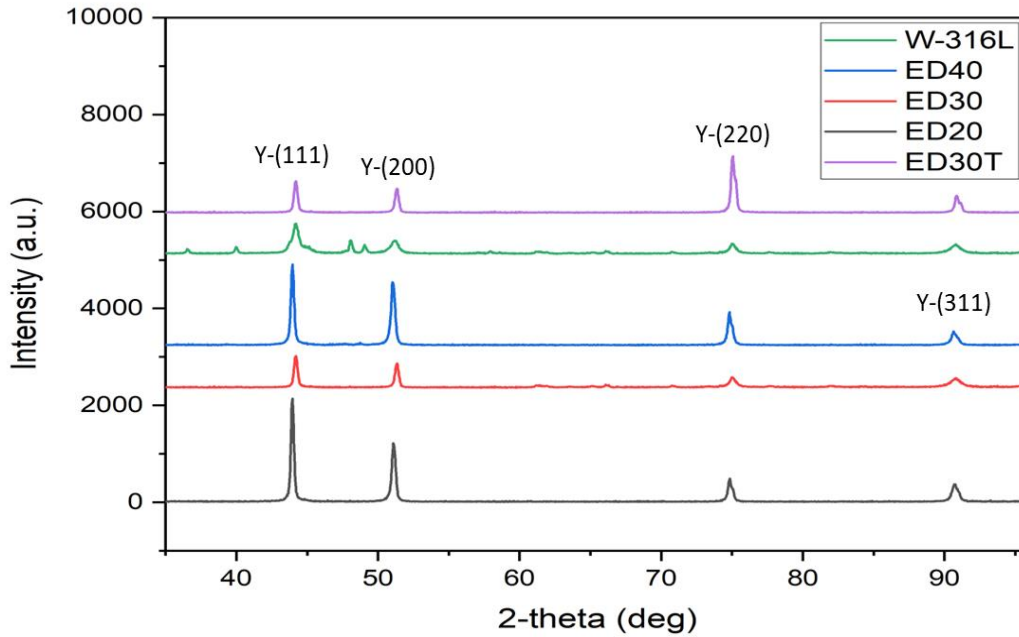


Figure 22: XRD results of the fabricated SLM samples as well as the wrought sample.

5.3 Corrosion Behavior in room temperature NaCl

The open circuit potential (OCP) measurement was used to keep track of the sample's corrosion potential when no external current was applied. The system is expected to reach a steady state when the potential is no longer affected by how long the sample was immersed. Figure 23 shows the OCP (E_{corr}) for SLMed and wrought 316L samples in 3.5% NaCl at different pH levels. At all pH levels, the E_{corr} of all specimen substrates goes up, and compared to ED20, there is a big change in the direction of the E_{corr} . The increase in E_{corr} is also due to the formation of a passive layer on the surface of the specimen substrates, which protects them from further corrosion. This suggests that the sample substrates are resistant to corrosion, which means they can be used in harsh environments. The OCP of ED30T, ED40, and W-316L was the best at pH 1, and their E_{corr} values are close to being even better than the same

samples at pH 3. But the open circuit potentials of some of them moved more toward positive values in the pH 5 and pH 7 solutions than in the acidic solution. It should be noted that the shift of the E_{corr} of high relative density substrates to more noble values shows that the substrate's resistance to corrosion susceptibility has improved in a noticeable way. This means that the high relative density substrates have become more resistant to corrosion in neutral and alkaline environments. This improvement in corrosion resistance is particularly significant, as it indicates that these substrates can withstand a wider range of pH conditions without undergoing significant degradation. Additionally, the shift towards more noble values suggests that the protective oxide layer on the substrate's surface has become more stable and effective in preventing corrosion. The high relative density means that the energy density must have had a big effect on both anodic and cathodic polarization. Anodic and cathodic polarization are two important electrochemical processes that occur during corrosion. Anodic polarization refers to the oxidation reaction at the anode, where metal atoms lose electrons and form metal ions. Cathodic polarization, on the other hand, involves reduction reactions at the cathode, where species such as oxygen or hydrogen ions gain electrons. These processes play a crucial role in determining the overall corrosion rate and potential of a substrate.

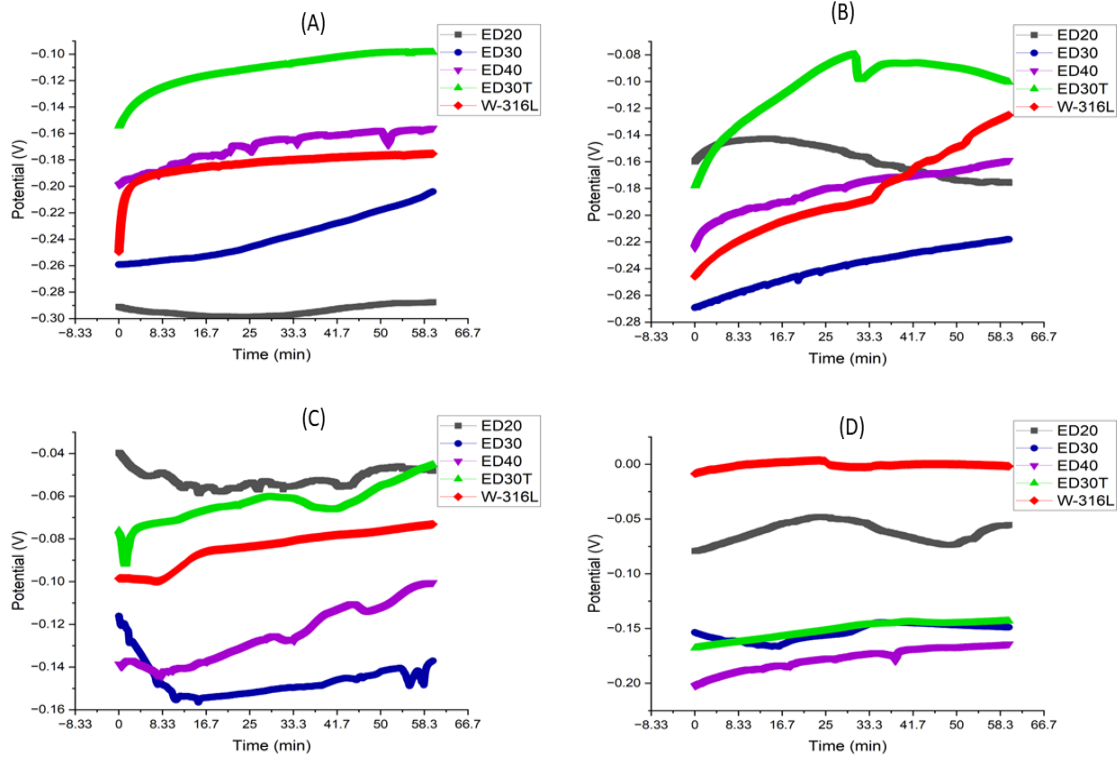


Figure 23: Open circuit potential of all specimens in 3.5 % NaCl solution A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5

Figure 24 and Figure 25 show LPR plots of SLMed and wrought samples in 3.5% NaCl solution at four pH levels. Figure 24 includes the curve of ED20 while it was removed in figure 25 to have a clear view for the others samples and a good comparison. According to the Stern Geary equation (4.5) and from the obtained LPR plots, the electrochemical parameters, including the polarization resistance (R_p) corrosion current density (I_{corr}), and corrosion rate, were calculated and the obtained values are shown in Table 8. As the energy density increased from 21 J/mm³ to 33 J/mm³, the R_p increased, while when the energy density reached 44 J/mm³, the R_p decreased. The same trend was observed for the relative density as well. These results suggest that there is an optimal

energy density range for achieving the highest Rp and relative density values in the material. In addition to that, the Rp and relative density reached the highest value after stress relief for ED 30 (ED30T). This indicates that the stress relief process can enhance the corrosion resistance of the 3D printed material. Further studies can be conducted to determine the optimal energy density and stress relief conditions for achieving the desired mechanical properties and corrosion resistance in the SLMed material.

The LPR plots of ED30T showed higher polarization resistance and lower corrosion current density compared to the wrought samples and other SLMed samples, indicating better corrosion resistance. On the other hand, the curves showed that the ED20 sample corroded the most quickly at all pH levels. This can be linked to the low energy density, which leads to unmelted powder and high porosity [74].

In contrast with relative density, Figure 26 shows corrosion rate versus relative density extracted from LPR results. When the relative density increased, the corrosion rate decreased at pH 1. ED-30T has the lowest corrosion rate and is 35 % better compared to the wrought sample W-316L. The ED30T sample's resistance to corrosion was improved because of the stress relief process in addition to its slower rate of cooling during the SLM process. This facilitated the formation of a more compact and protective surface film. Based on the obtained corrosion current density (I_{corr}) values and corrosion rate at pH 1, the corrosion resistance of the samples from high to low is characterized as follows: ED30T > ED40 > W-316L > ED30 > ED20. To establish a correlation between the microstructure and the corrosion rate, ED30T has a more refined microstructure compared to the other samples. The refined microstructure leads to a higher density of grain

boundaries, which can act as barriers to prevent the penetration of corrosive species into the material. This may help us understand why ED30 is more resistant to corrosion than ED20. It's also possible for corrosive species to move more easily through ED30T because it has more grain boundaries than W-316L and ED40. This slows down the corrosion rate even more.

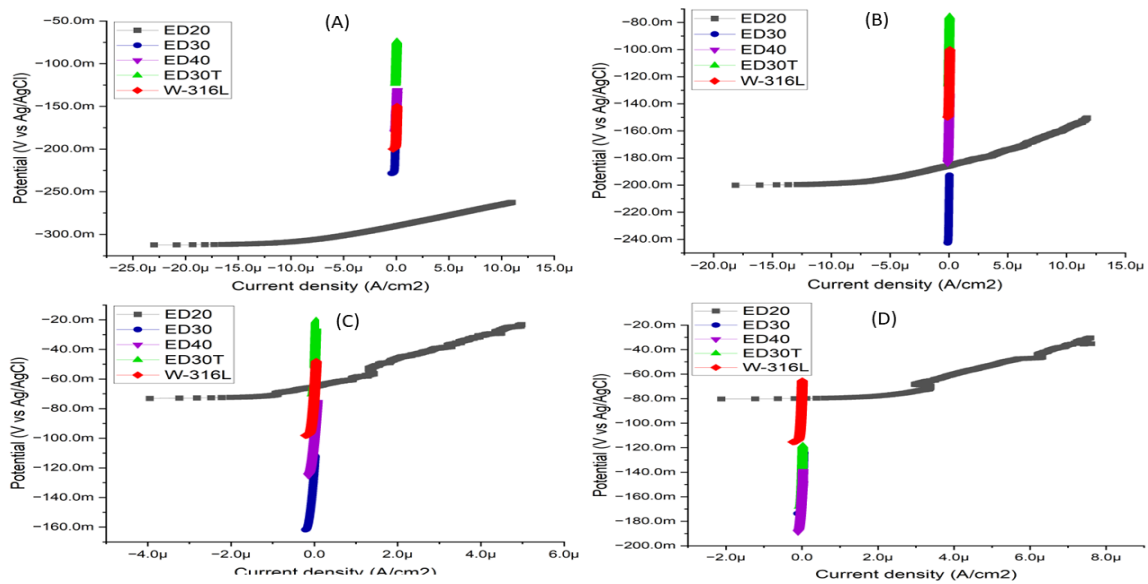


Figure 24: Linear Polarization Resistance (LPR) of all specimens in 3.5 % NaCl solution A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5.

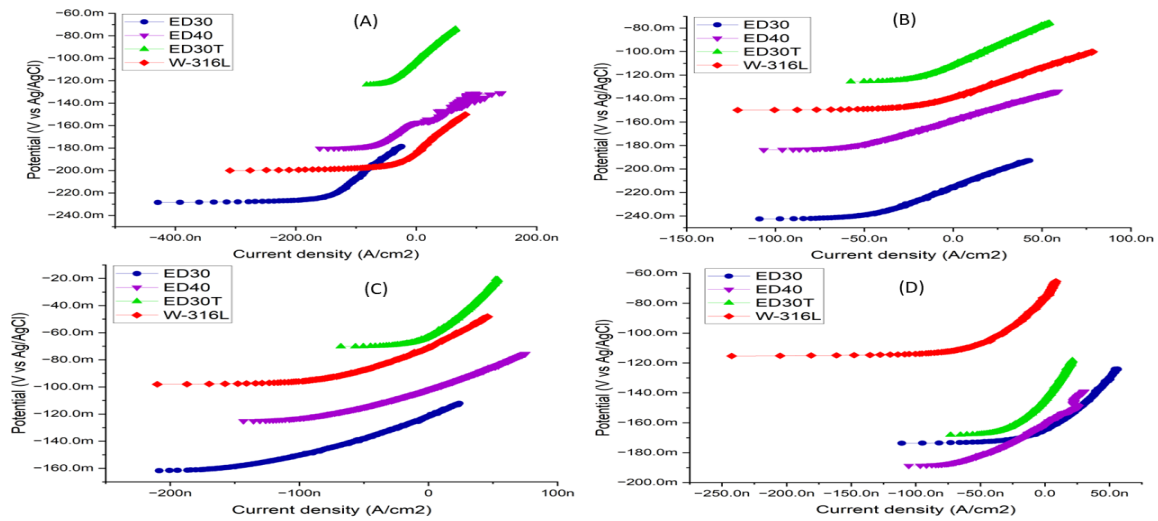


Figure 25: Linear Polarization Resistance (LPR) of all specimens in 3.5 % NaCl solution A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5. without ED-20.

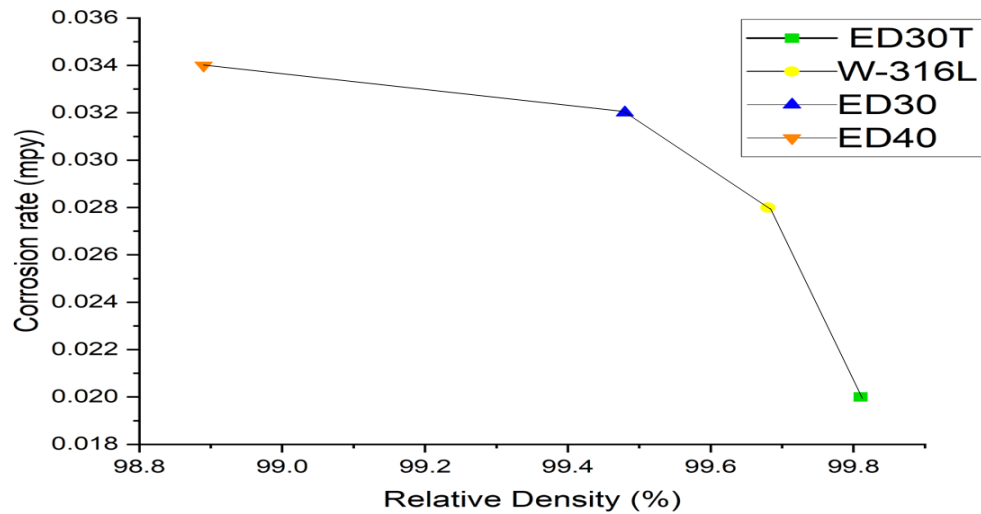


Figure 26: Corrosion rate versus Relative density extracted from Linear Polarization Resistance (LPR) results in 3.5% NaCl solution at pH 1.

Table 8 Polarization resistance (Rp), corrosion current density (Icorr), and corrosion rate obtained from Linear Polarization Resistance (LPR) plots.

pH	Sample IDs	Icorr μA	Ecorr mV	CR mpy	Rp $\text{k}\Omega.\text{cm}^2$	Eff %
1	W-316L	0.10	-158.17	0.044	308.6	
	ED20	0.14	-289.1	6.612	1.80	-52%
	ED30	0.11	-178.6	0.05	238.8	-15%
	ED30T	0.06	-102.85	0.028	420.65	35%
	ED40	0.08	-157.45	0.037	322.5	14%
3	W-316L	0.09	-147.88	0.028	332.75	
	ED20	0.2	-184.45	7.304	1.634	-130%
	ED30	0.06	-215	0.032	449.15	33%
	ED30T	0.04	-112.1	0.02	584.1	49%
	ED40	0.07	-158	0.034	353.85	15%
5	W-316L	0.1	-98.09	0.047	194.35	
	ED20	0.46	-63.14	2.112	6.352	-354%
	ED30	0.14	-122.35	0.066	182.95	-42%
	ED30T	0.05	-63.33	0.024	498.65	48%
	ED40	0.12	-102	0.055	217.95	-18%
7.5	W-316L	0.05	-50.56	0.022	208.43	
	ED20	0.18	-79.03	2.101	6.584	-277%
	ED30	0.07	-164.8	0.032	381.5	-41%
	ED30T	0.04	-143.5	0.018	659	19%
	ED40	0.07	-161	0.034	354	-51%

Electrochemical Impedance Spectroscopy (EIS) was used to study the passivation layer of SLMed and wrought samples for corrosion resistance evaluation as it is also capable of providing information relating to the reaction parameters, corrosion rates, oxide formation and their characteristics, surface integrity, porosity, and other interfacial properties [75]. Figure 277 shows the equivalent circuit used to fit EIS data in this study to investigate the characteristics of the

electrochemical process. R_s represents the electrolyte resistance in this circuit, whereas CPE_f and R_f represent the capacitance and resistance of the oxide layer on the samples, respectively. Cdl is the double-layer capacitance at the film–solution interface, and R_{ct} is the charge-transfer resistance for the adsorption of hydroxide species at the film–solution interface.

The fitted experimental results for the modulus, phase angle, and Nyquist plots are displayed in figure 28 and figure 29. It is evident that in NaCl solutions, the blank substrate exhibited just a one-time constant. This may be attributed to the capacitive behavior of the double layer (Cdl) in parallel with the charge transfer resistance (R_{ct}), which results from corrosion of the metallic substrate. However, the Bode diagrams reveal a two-time constant, which becomes increasingly apparent with longer exposure times. As evidenced by the two maxima found in the phase angle plot of the Bode diagram, this phenomenon occurs in the low-frequency area for the NaCl solution.

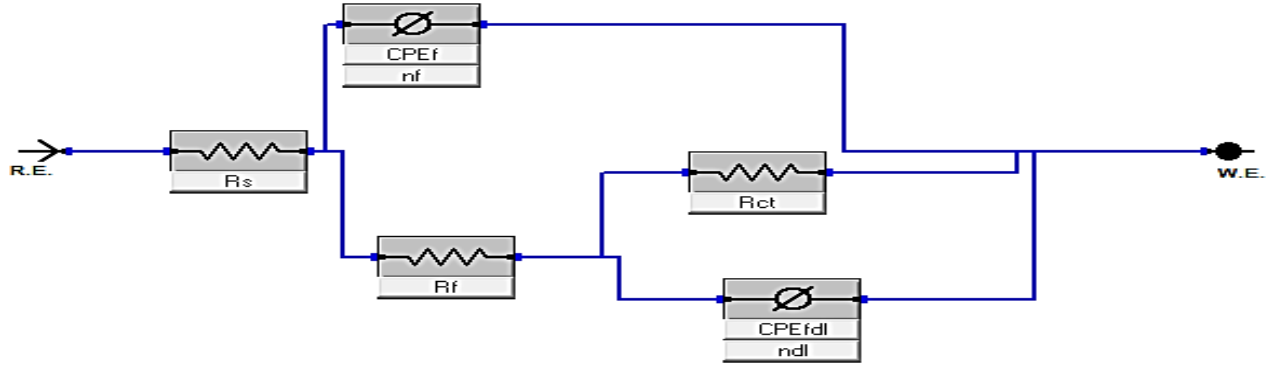


Figure 27 Equivalent circuit used to fit EIS data.

Table 9 represent the optimum EIS parameters for W-316L, ED20, ED30, ED40, and ED30T in 3.5 % NaCl solutions at four pH levels. ED30T has better corrosion resistance compared to the other samples. It is 52 % higher than the wrought sample W-316L at pH 1. However, the steady-

state film thickness (L_{ss}) has no significant difference from other samples.

Using Eq 5.1, the steady-state film thickness (L_{ss}) might be determined from the film's capacitance [76]:

$$L_{ss} = \frac{\varepsilon \varepsilon_0 A}{C_f} \quad (5.1)$$

Where ε is the relative permittivity of the passive film (usually taken as 15.6 for Cr_2O_3) [63], ε_0 is the vacuum permittivity ($8.8549 \times 10^{-14} \text{ Fcm}^{-1}$), A is the electrode surface area (1 cm^2), and C_f is the capacitance of the passive film obtained by the optimization of the EIS. Based on the calculation, it was determined that the thickness of the passive film did not change considerably with the energy density and that it was around 1 nm. Because of the significant presence of porosity and voids, the ED20 exhibited the lowest values for both the passive film resistance and the charge-transfer resistance. This phenomenon was ascribed to the extensive presence of porosity and voids. However, the ED30T shows the thicker passive film resistance at all pH values, followed by W-316L. The thicker passive film resistance observed in ED30T and W-316L suggests that these materials have a higher resistance to corrosion compared to ED20. This could be attributed to their reduced porosity and voids, resulting in a more compact and protective passive film layer. Additionally, the higher energy density used in the ED30T process might have contributed to the formation of a thicker passive film.

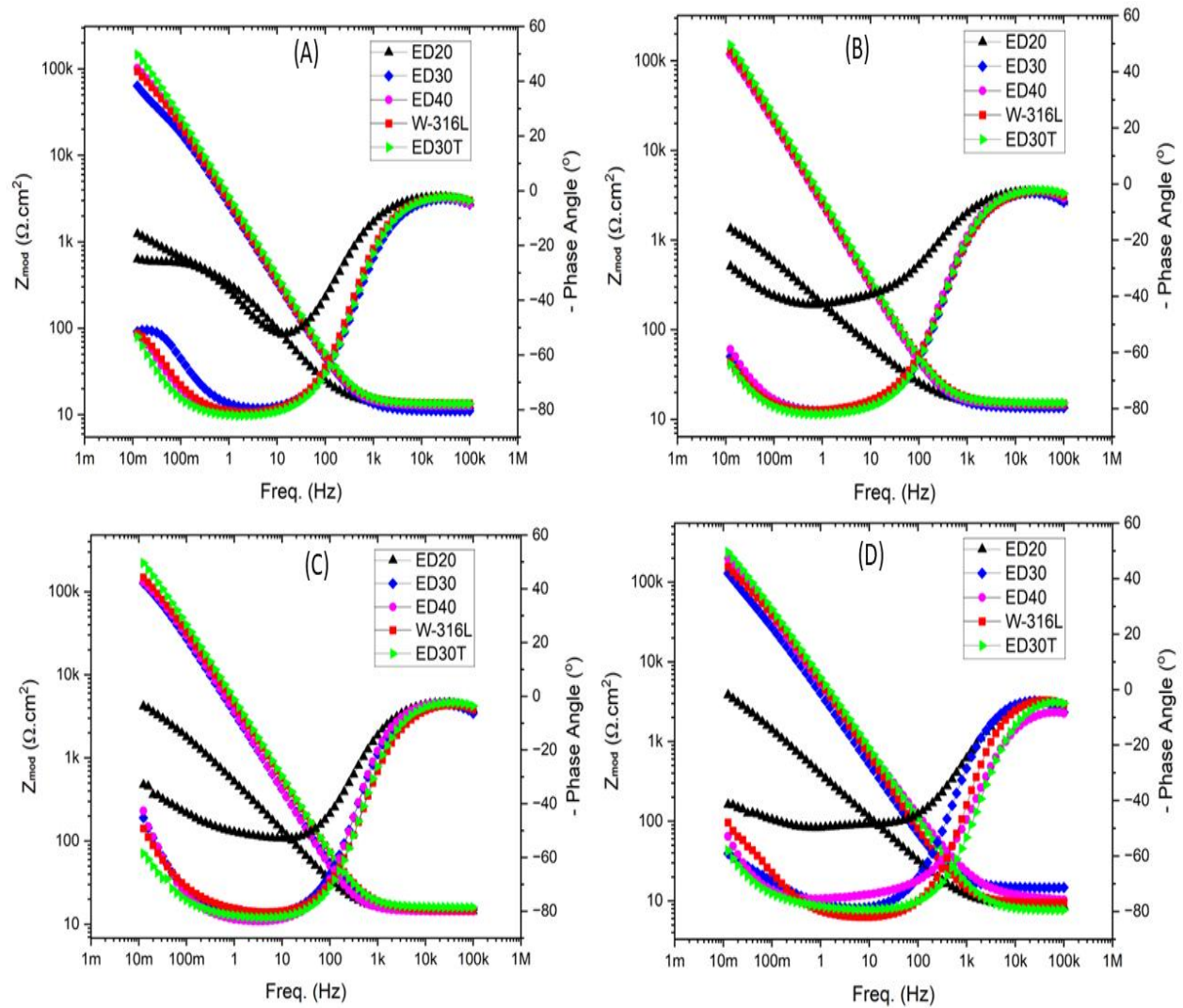


Figure 28 Electrochemical impedance spectroscopy (EIS), Bode plots of all specimens in 3.5 % NaCl solution

A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5.

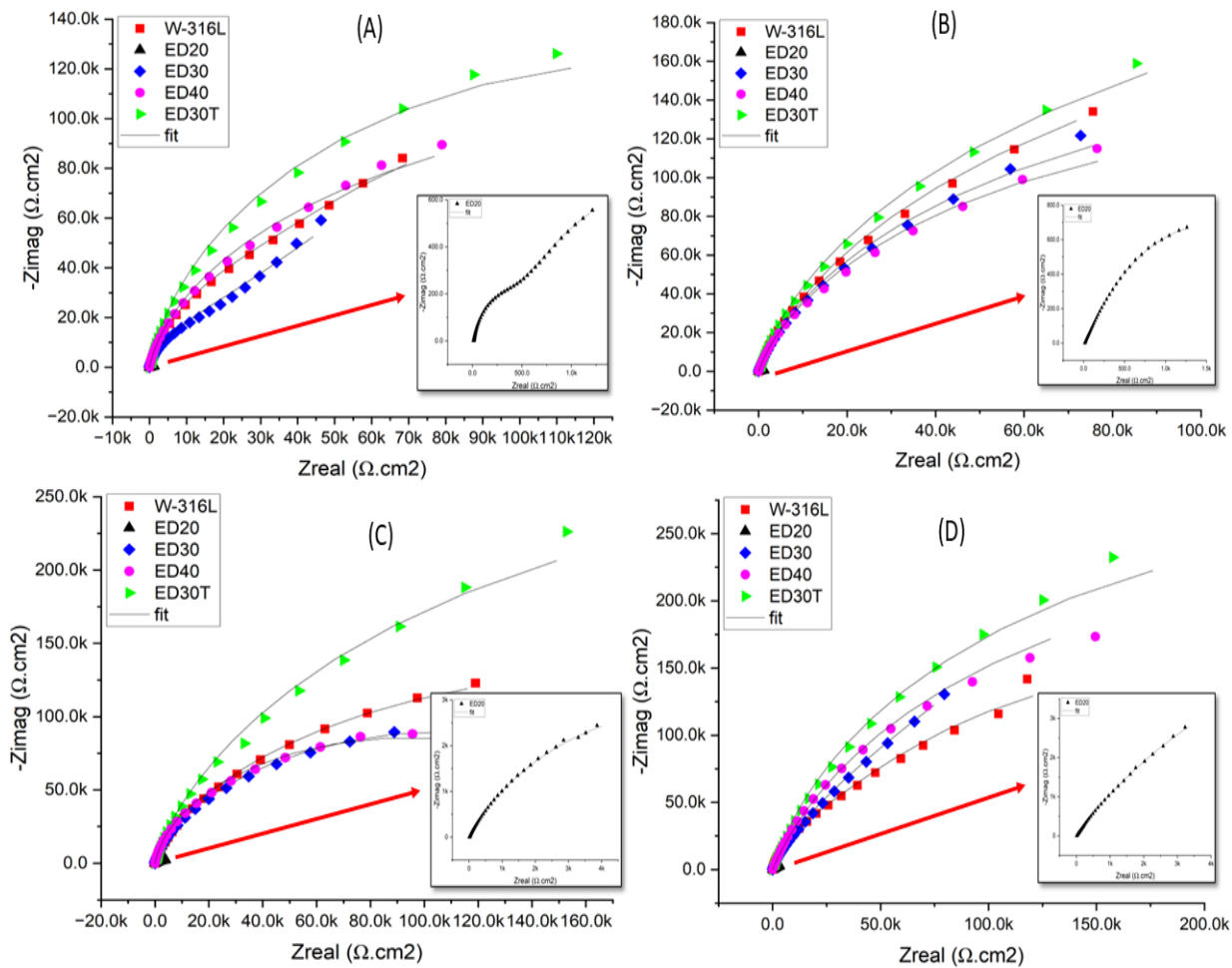


Figure 29 Electrochemical impedance spectroscopy, Nyquist plots of all specimens in 3.5 % NaCl solution A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5.

Table 9 Electrochemical impedance spectroscopy data of all specimens in 3.5 % NaCl solution at four pH values.

pH	Sample IDs	Rs	Rct	CPEFdl	ndl	Rf	CPEf (Cf)	nf	Rt(Rct+Rf)	X2	%
		Ω .cm2	K. Ω .cm2	μ F/cm2		K. Ω .cm2	μ F/cm2		K. Ω .cm2		
1	W-316L	13.61	124.8	1.67E-04	1	122.1	6.5E-05	0.91	246.9	3.26E-04	
	ED20	12.59	2.92	3.01E-03	0.5	0.43	4.34E-04	0.76	3.3	2.31E-04	-97.26%
	ED30	11.21	294.25	8.62E-05	0.66	44.14	7.02E-05	0.9	338.4	8.68E-04	37.06%
	ED30T	13.5	97.24	3.25E-07	0.01	280.4	5.57E-05	0.92	377.6	4.26E-04	52.95%
	ED40	12.76	231.67	3.88E-05	0.43	116.7	6.45E-05	0.91	348.4	5.08E-04	41.10%
3	W-316L	12.3	213.4	2.75E-12	0.38	0.16	7.02E-05	0.9	213.6	7.80E-04	
	ED20	14	2.9	1.41E-03	0.5	0.09	7.55E-04	0.68	3	4.17E-04	-98.59%
	ED30	13.6	2	3.56E-09	0.01	335.3	7.32E-05	0.9	337.3	8.75E-04	57.96%
	ED30T	15.3	464.8	9.44E-06	0.9	0.13	5.30E-05	0.92	464.9	2.20E-04	117.70%
	ED40	14.7	1.47E-07	6.45E-04	0.01	294.6	7.55E-05	0.9	294.6	7.14E-04	37.95%
5	W-316L	15	170.8	8.19E-06	0.381	0.96	5.38E-05	0.94	171.8	3.23E-04	
	ED20	14.2	12.4	5.15E-04	0.484	0.13	2.09E-04	0.8	12.5	3.08E-04	-92.70%
	ED30	15	50.49	1.34E-04	0.998	157.7	5.33E-05	0.92	208.2	6.01E-04	21.20%
	ED30T	16	415.7	8.83E-06	0.69	187.7	3.57E-05	0.93	603.4	3.26E-04	251.30%
	ED40	14.2	190.8	1.28E-12	0.01	0.06	5.12E-05	0.93	190.9	1.00E-03	11.10%
7.5	W-316L	9.49	284.4	3.94E-05	0.82	109.8	3.28E-05	0.92	394.2	4.18E-04	
	ED20	7.78	19.8	2.16E-05	0.92	2.78E-03	8.81E-04	0.55	19.8	3.75E-04	-94.97%
	ED30	14.65	433.4	1.44E-05	0.45	55.2	4.79E-05	0.89	488.6	9.80E-04	23.95%
	ED30T	7.57	8.71E-07	5.77E-04	0.02	601.8	3.22E-05	0.88	601.8	7.54E-04	52.66%
	ED40	10.79	9.24E-02	3.57E-06	0.28	552.4	3.90E-05	0.84	552.5	2.68E-03	40.16%

The Cyclic Potential Dynamic Polarization (CPDP) test was performed to get a better understanding of the corrosion behavior of the 3D-printed stainless steels. Figure 30 depicts the CPDP curves for several energy density samples and wrought 316L samples: ED-20, ED-30, ED-30T, ED-40, and wrought 316L. The corrosion potential (E_{corr}), corrosion current density (i_{corr}), repassivation potential (E_{rep}), and corrosion rate (in mpy), were extracted data from the CPDP curves using the Tafel slope in 3.5% NaCl solution at four different pH levels. Table 10 summarizes the results of the CPDP curve for all specimens.

CPDP curves demonstrate that 3D printed samples ED-30 & ED30T have higher E_{pit} values when compared to wrought sample W-316L at pH 1. These 3D printed samples have much higher E_{pit} values at pH 3 about 300 mV from wrought W-316L which is similar to the reported E_{pit} value by Sander, et al. [42] in his study. The E_{pit} is defined as the potential at which the surface passive film breakdown occurs as indicated by the rapid increase in the current in the active-passive region [77]. However, the E_{pit} values of 3D printed samples have no significant difference from the wrought sample W-316L at pH 5 & pH 7.5 but still, they are higher than W-316L. The reason is the correlation between pH value and the intensity of corrosive ions (such as Cl) in the acid media. An increase in the pH value will supplement the activity of corrosive ions. Also, it was reported by Prawoto, et al. [78] that when the acidity of the solution increase (lower pH), the corrosion rate will increase and its impact will be more significant at $pH < 3$. This can conclude that the 3D printed samples have a more stable passive film and better corrosion resistance than the wrought sample at lower pH values.

In this study, all SLMed samples had a higher E_{pit} values than wrought 316L stainless steel, except

ED-20. In contradiction to this study, Kazemipour, et al. [79] detected that there is no significant correlation between E_{cor} and i_{cor} and porosity percentage. However, it was found in this study that an increase in the porosity led to a decrease in the re-passivation potential for samples like ED-20 which had the lowest re-passivation value. Moreover, ED-20 has the lowest corrosion potential (E_{corr}) and pitting potential (E_{pit}) at all pH values. Furthermore, repassivation potential (E_{rep}) values were found to be the lowest showing how the porousness of the specimen impacts E_{rep} . The repassivation potential (E_{rep}) values will decrease with an increase in the porosity of the specimen. At pH-1, the E_{corr} of ED-30T is moved to higher potentials than those of the other samples, indicating that they are less susceptible to corrosion. However, there is a slight difference in the corrosion potential (E_{corr}) between ED-30, ED-30T, ED-40, and wrought 316L at pH 3, pH 5, and pH 7.5. Finally, It was also detected that the 3D printed samples with high relative density and high energy density enable better pitting corrosion resistance than the wrought specimen W-316L in an acidic environment.

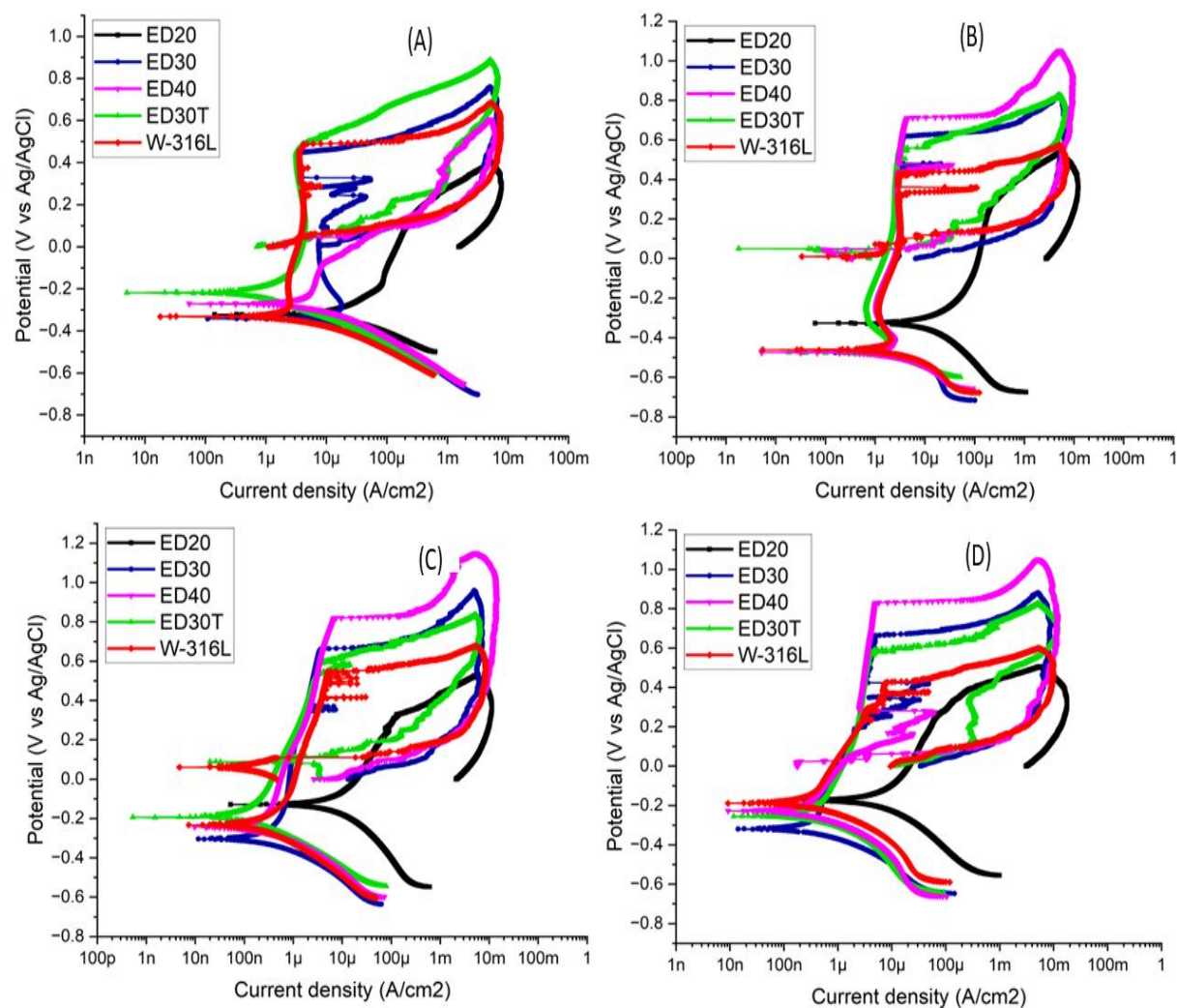


Figure 30 Cyclic potentiodynamic polarization curves at 3.5 % NaCl solution at four different pH values. A) at pH 1 B) at pH 3 C) at pH 5 and D) at pH 7.5

Table 10 The results of Tafel fitting extract from CPDP curve at pH1, pH3, pH5, and pH7.5 solution.

pH	Sample IDs	Beta A mV/dec	Beta C mV/dec	Icorr $\mu\text{A}/\text{cm}^2$	Ecorr mV	CR mpy	Eff %	Ipit μA	Epit mV	Erep mV	Epit- Erep
1	W-316L	7.5E+14	0.08	2.13	-307.0	2.78	-	3.35	423.10	71.43	351.6
	ED20	5.3E-01	0.17	13.5	-322.0	17.5	-533%	236.5	115.4	-208.8	324.2
	ED30	1.0E+15	0.11	5.95	-343.0	7.75	-179%	3.57	439.60	5.49	434.11
	ED30T	4.0E+14	0.22	1.35	-248.6	1.75	36%	3.93	494.50	60.95	433.55
	ED40	3.3E+14	0.10	2.76	-271.0	3.60	-29%	746.40	285.70	93.40	192.30
3	W-316L	4.0E+14	0.11	1.19	-461.00	1.55		2.70	340.7	170.3	170.40
	ED20	5.85E-01	0.50	8.53	-326.00	11.08	-617%	198.5	263.7	-186.8	450.50
	ED30	1.0E+15	0.09	1.22	-474.00	1.02	-2.3%	3.74	615.40	-5.35	620.75
	ED30T	8.15E-01	2.E+14	0.08	-457.53	0.14	93%	3.74	653.20	10.99	642.21
	ED40	5.0E+14	0.05	1.87	-238.12	0.67	-57%	4.60	696.40	43.96	652.44
5	W-316L	3.67E-01	0.16	0.16	-174.60	0.21		4.97	554.90	104.40	450.50
	ED20	5.12E-01	0.27	0.47	-129.00	6.08	-188%	128.80	329.70	126.20	203.50
	ED30	1.35E+00	0.14	0.18	-304.00	0.23	-11%	3.46	653.80	-104.0	758.20
	ED30T	2.00E+14	0.22	0.13	-210.00	0.17	20%	4.04	604.00	120.90	483.10
	ED40	1.96E+00	0.14	0.13	-244.00	0.18	17%	6.69	806.30	-10.99	817.29
7.5	W-316L	5.94E-01	0.09	0.08	-187.60	0.11		3.10	489.00	-10.49	499.49
	ED20	6.29E-01	0.26	0.29	-174.00	5.63	-248%	71.50	258.20	-169.30	427.50
	ED30	7.57E-01	0.10	0.13	-319.00	0.17	-57%	5.02	659.30	-142.90	802.20
	ED30T	4.49E-01	0.09	0.05	-191.40	0.07	38.%	5.40	604.40	6.42	597.98
	ED40	3.76E-01	0.11	0.11	-228.00	0.14	-32%	5.20	833.40	-4.60	838.00

Figure 31 depicts the corrosion rate (mpy) of all specimens vs pH levels. Compared to the other samples, ED30T exhibits a significantly low corrosion rate at pH 1 and pH 3, and a slight corrosion rate difference at pH 5 and pH 7. Compared to the wrought W-316L specimen, ED-30T shows a 36% greater corrosion resistance at pH 1. This suggests that ED-30T could be a more suitable material for applications in acidic environments where corrosion is a concern. Further research could investigate the long-term durability of ED-30T under these conditions and explore its potential for use in industries such as chemical processing or oil and gas. There is a strong correlation between corrosion rate and pH. The corrosion rate of SLMed and wrought 316L stainless steel increases as the pH level decreases. This is because the acidic environment enhances the dissolution of the protective oxide layer on the surface of the steel, leading to increased corrosion. Therefore, it is important to maintain a neutral or slightly basic pH to minimize corrosion in stainless steel [78].

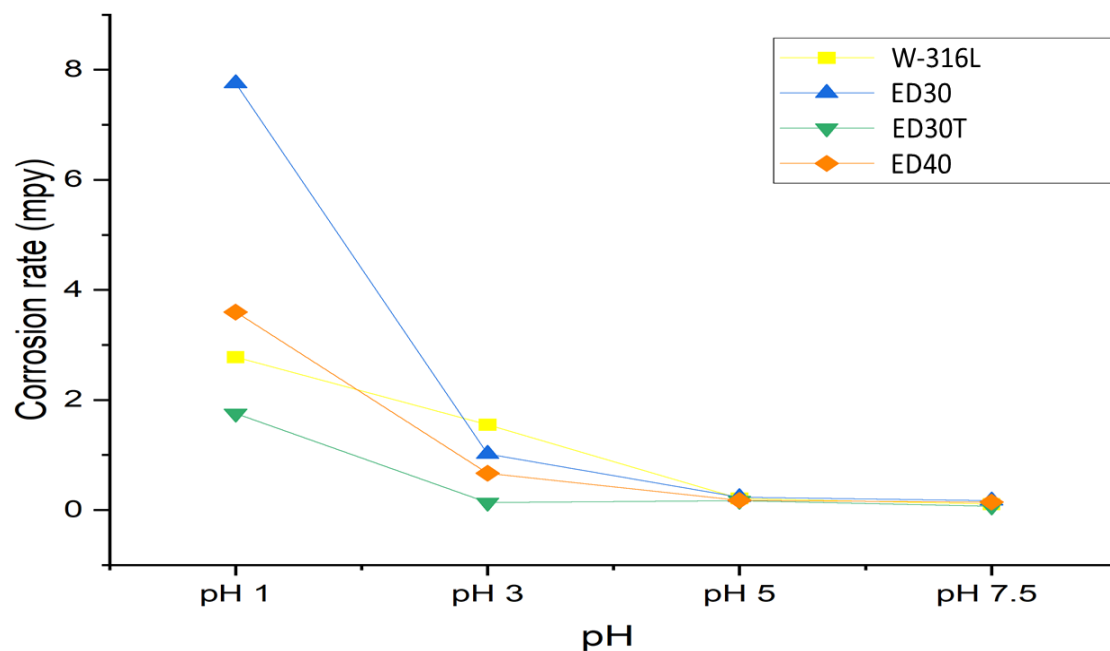


Figure 31 Corrosion rate of studied samples at different pH values based on CPDP Curves.

In order to determine the level of damage, the EDS and SEM surface morphology of the corroded area of SLMed 316L and wrought 316L samples immersed in 3.5% NaCl medium were examined. The micrographs of the samples at pH 1 are depicted in figure 32. It was observed that at pH 3, pH 5, and pH 7.5 values, all specimens indicated less damage compared to pH-1 after the electrochemical corrosion test. Considering this, the present study focused on the EDS & SEM analysis of all specimens in 3.5 % NaCl at pH 1 only. The results of EDS & SEM analysis at pH 1 showed that the specimens had significant pitting corrosion and severe damage on their surfaces. Therefore, it can be concluded that pH 1 has a more detrimental effect on the corrosion behavior of the specimens compared to other pH values tested in this study.

The pitting and porosity were found to be more prevalent on ED 20 because of the low energy density thereby leading to an inefficient melting of the powder and porosity. On the other hand,

less pitting was observed on ED 30T with a high energy density and the lowest porosity. Formation of deep and wide caves was observed on ED 30T & W-316L with corrosion products.

Figure 33 and figure 34 show the morphology and the EDS spectrum results for the pitting of ED30T and W-316L, respectively. Also, it was assumed that the pit on ED30T and W-316L takes the shape of the grains or crystallites. For example, in ED 30T the shape of the pit is shallow and wide, while in W-316L pit shape is deep and narrow. This could be due to the shape of the grains and the ability of the SLMed sample to repassive faster than the wrought sample. In addition, in EDS results, it was observed for all specimens that around each pit there is a high concentration of NaCl limited to the pit itself. Lastly, for ED 30T, the wrought sample W-316L had the best corrosion resistance as evidenced by the SEM images.

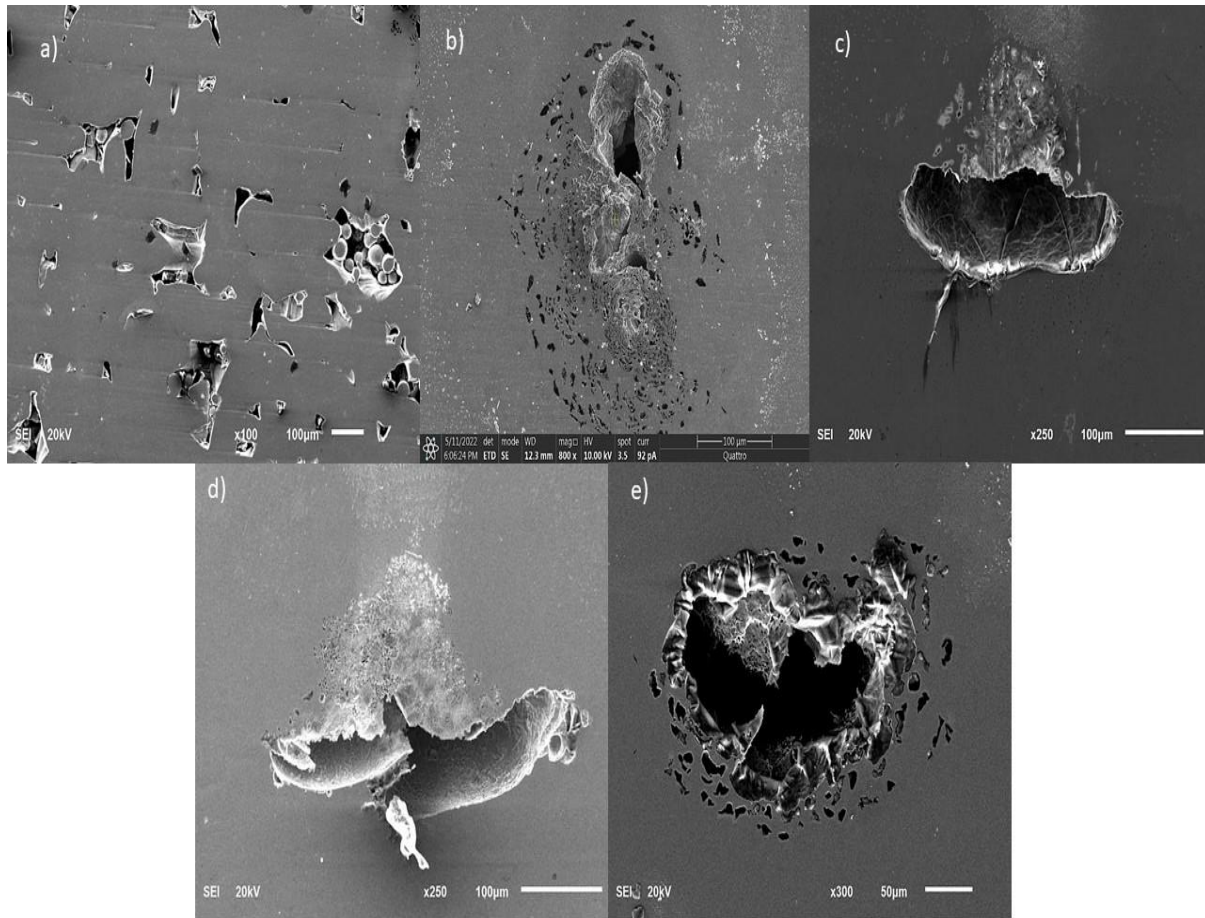


Figure 32: SEM image for pits on a) ED20 b)ED30 c) ED40 d) ED30T e) W-316L immersed in 3.5% NaCl solution at pH 1

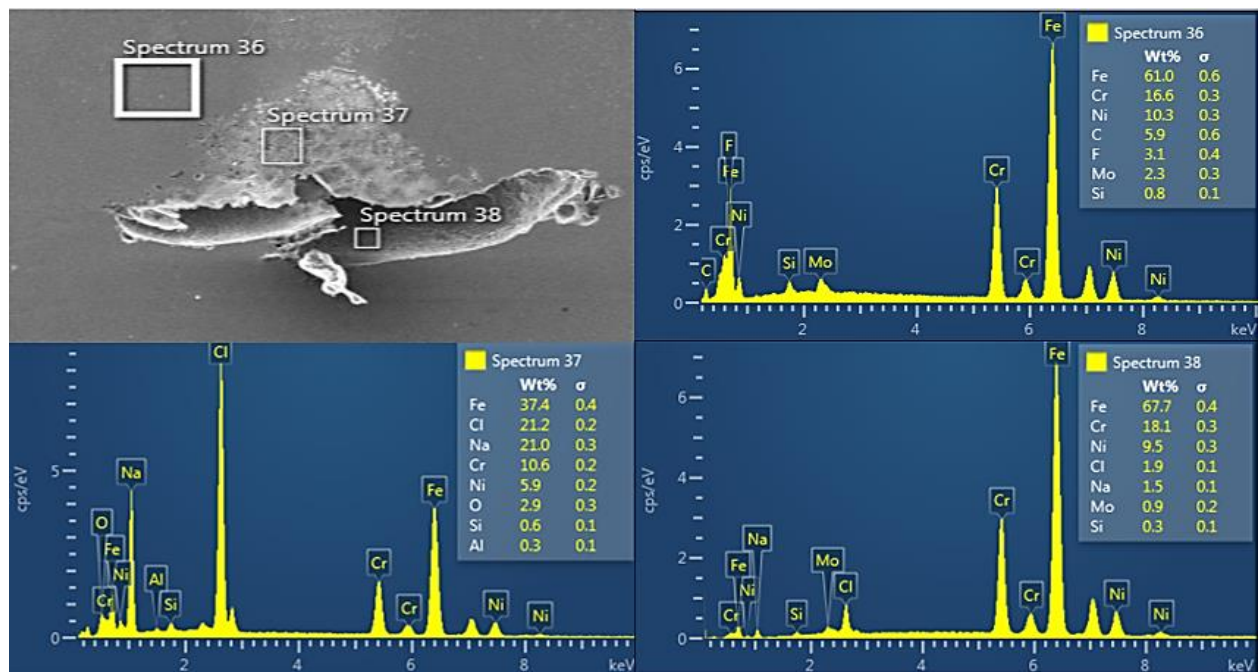


Figure 33 EDS results for ED 30T pit

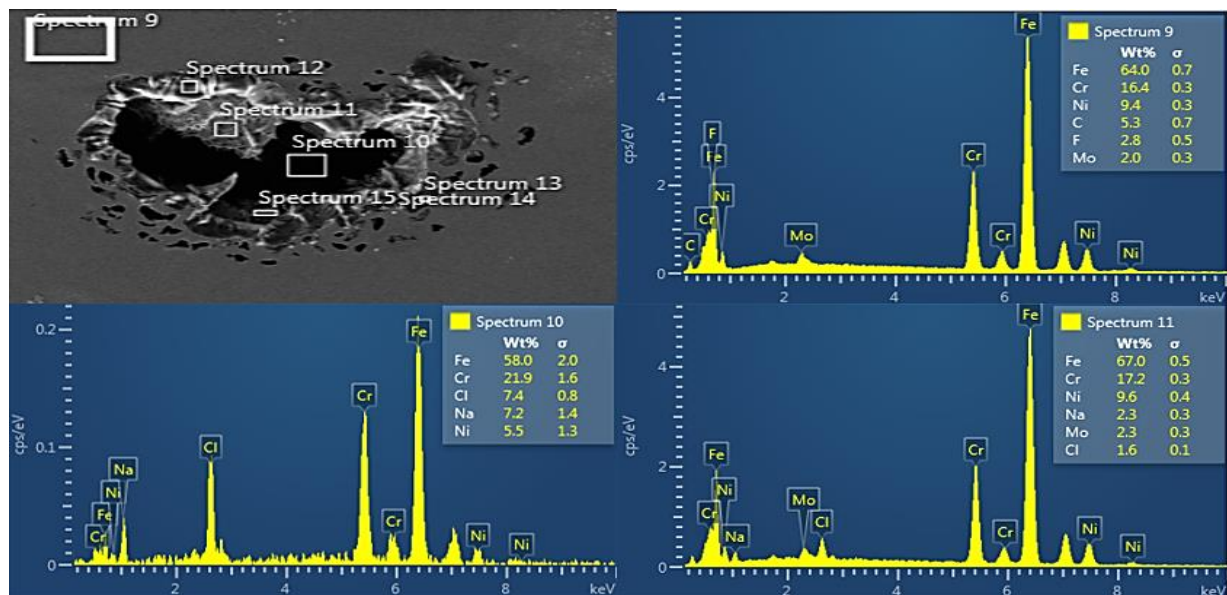


Figure 34 EDS results for W-316L pit

5.4 Corrosion behaviour at high temperature NaCl

Figure 35 shows the variation of E_{corr} with time for SLMed 316L and wrought 316L samples in 3.5 % NaCl at room temperature and 70 °C. At room temperature, the E_{corr} of both specimen substrates reached equilibrium, with a significant shift in the E_{corr} towards the nobler direction compared to the same samples at temperature of 70 °C. It can be noted that the temperature had a big effect on both anodic and cathodic polarization. The open circuit potential of ED30T was more noble at room temperature which indicate a noticeable improvement of the substrate resistance to corrosion susceptibility.

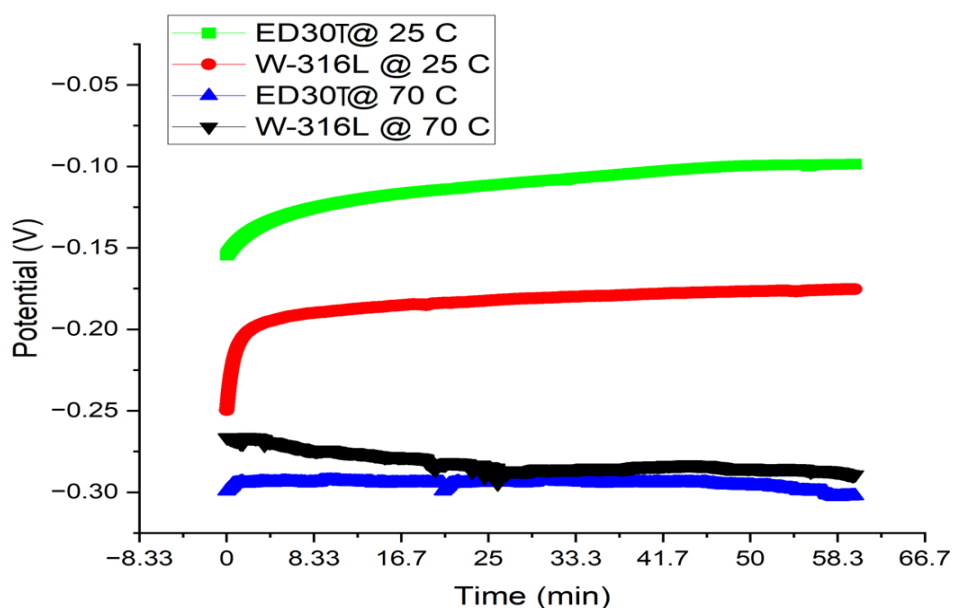


Figure 35: Open circuit potential (OCP) of SLMed 316L and wrought 316L at room temperature and 70 °C.

Figure 36 shows LPR plots of SLMed 316L and wrought 316L samples in 3.5 % NaCl at room

temperature and 70 C. Table 11 shows the polarization resistance (R_p), corrosion current density (I_{corr}), and corrosion rate that obtained LPR. [74]. At both low and high temperatures, ED30T samples exhibited lower I_{corr} values than the wrought 316L sample. In addition, the corrosion rates of ED-30T samples became more consistent and steadier as the exposure time rose. Moreover, the corrosion rate of the ED-30T samples was lower than that of W-316L, indicating that the 3D-printed samples exhibited superior corrosion resistance to the other samples across the temperature ranges.

Figure 37 shows the corrosion rates (mpy) of ED30T and W-316 at two temperatures in 3.5% NaCl solution. When compared to W-316L, ED30 had a much lower rate of corrosion at high temperatures and only a slight difference at room temperature. There is a significant correlation between the corrosion rate and the temperature. When the temperature increases, the corrosion rate also increases, as reported for wrought 316L stainless steel in previous literature [78], [80], [81]. In the case of ED30T and W-316, it can be seen that the temperature plays a major role in determining the corrosion rate. The higher temperature, the higher corrosion rates of both alloys, but ED30T still had better corrosion resistance than W-316, suggesting that ED30T is more resistant to corrosion at higher temperatures. At room temperature, ED-30T has a lower corrosion rate and is 35 % better compared to the wrought sample W-316L. This percentage increased to 99 % when the temperature increased, which indicates the SLMed 316L samples have better corrosion resistance at high temperatures than the wrought samples.

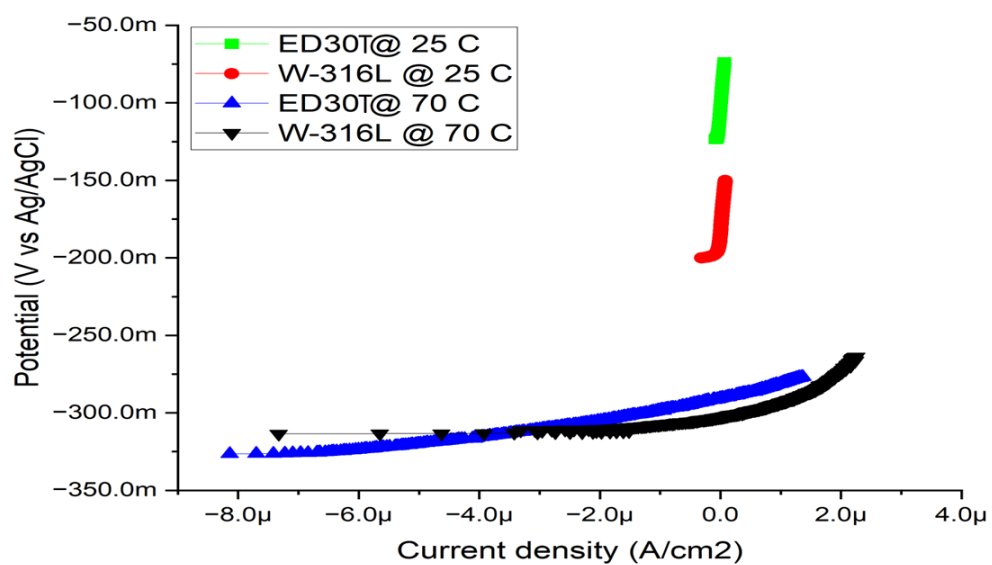


Figure 36: Linear Polarization Resistance (LPR) plots of SLMed 316L and wrought 316L samples in 3.5 % NaCl at room temperature and 70 C.

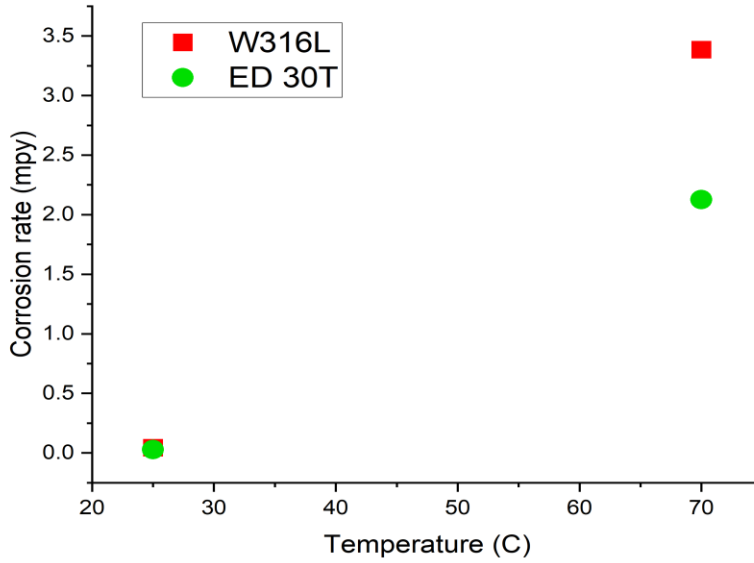


Figure 37: Corrosion rate versus temperature extracted from LPR results.

Table 11: Polarization resistance (R_p), corrosion current density (I_{corr}), and corrosion rate obtained from Linear Polarization Resistance (LPR) plots in 3.5 % NaCl solution at pH 1 room and 70 C temperature

T	Sample IDs	I_{corr} μA	E_{corr} mV	CR mpy	R_p k Ω .cm ²	Eff %
25 C	W-316L	0.10	-158.17	0.044	308.625	
	ED30T	0.06	-102.85	0.028	420.65	35%
70 C	W-316L	7.407	-304.05	3.3845	3.5665	
	ED30T	0.005	-290.05	2.127	5.6015	99.9%

The SLMed 316L and wrought 316L samples were tested twice for EIS in 3.5 pct NaCl solutions at room temperature and 70 C. Figure 38 displays the equivalent circuit used to fit EIS data to

evaluate electrochemical process parameters. In this circuit, R_s is the electrolyte resistance, CPE_f is the oxide layer capacitance, and R_f is the sample oxide layer resistance. Cdl is the film–solution interface double-layer capacitance, and R_{ct} is the charge-transfer resistance for hydroxide species adsorption.

Figures 39 and figure 40 show fitted modulus, phase angle, and Nyquist plots. The blank substrate had one time constant in NaCl solutions due to the capacitive behavior of the double layer (Cdl) and the charge transfer resistance (R_{ct}) from corrosion of the metallic substrate. With extended exposure times, Bode graphs show a two-time constant. In the NaCl solution’s low frequency Bode diagram, the phase angle plot shows two maxima points.

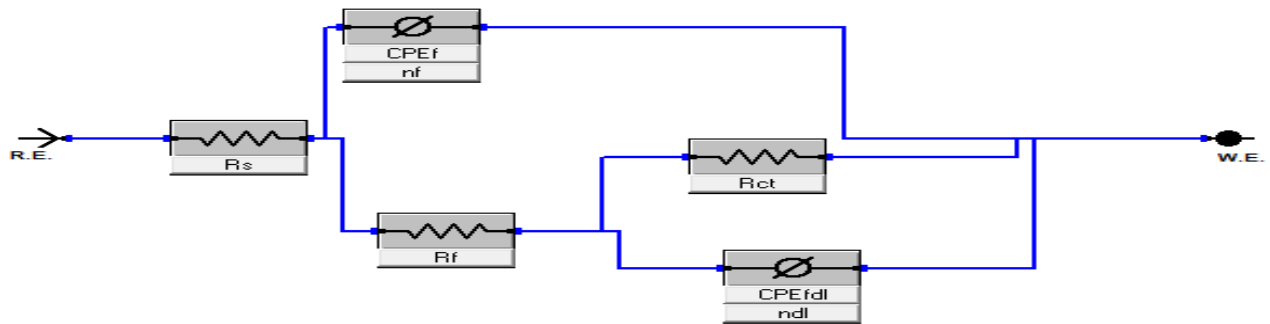


Figure 38:Equivalent circuit used to fit EIS data.

Tables 12 represent the optimum EIS parameters for W-316L ED30T in 3.5 pct NaCl solutions at two temperatures value. It can be seen that ED30 has better corrosion resistance compared to the W-316L. It is better by 52 % than the wrought sample W-316L in the room temperature while this percentage was reduced to 11 % at high temperature.

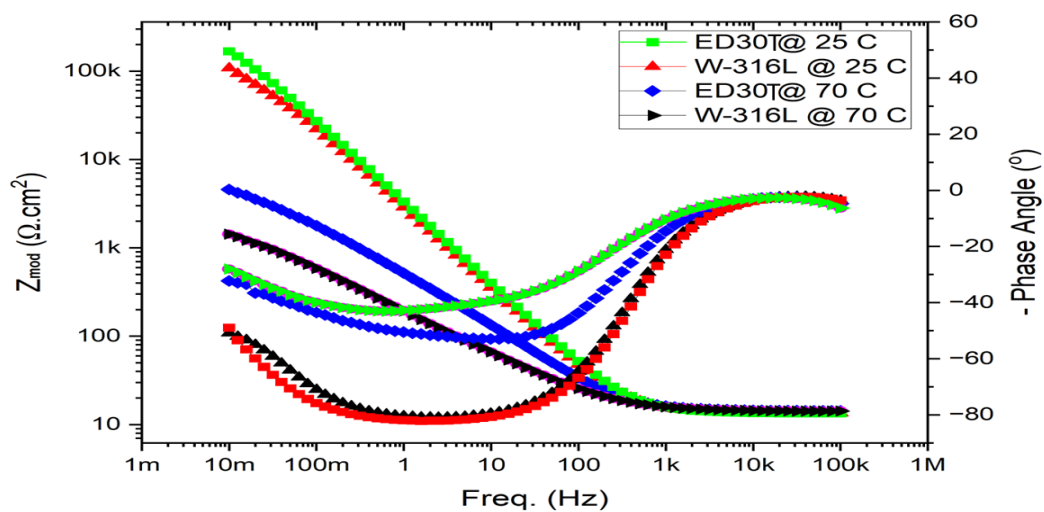


Figure 39: Electrochemical impedance spectroscopy (EIS), modulus of SLMed 316L and wrought 316L samples in 3.5 % NaCl at room temperature and 70 C.

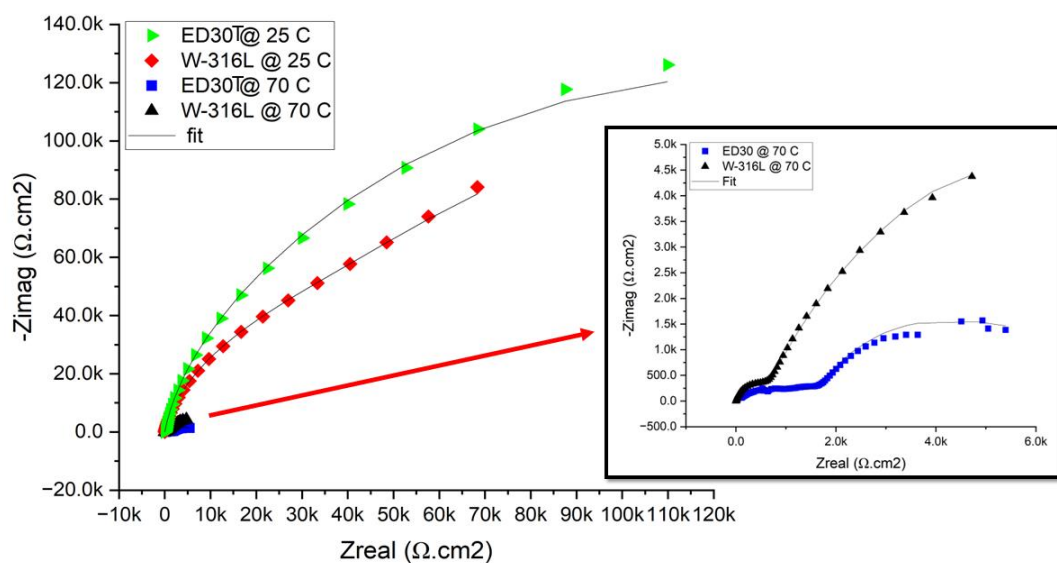


Figure 40: Nyquist plots of SLMed 316L and wrought 316L samples in 3.5 % NaCl solution

Table 12: Electrochemical impedance spectroscopy data of all specimens in 3.5 % NaCl solution at pH 1 room and 70 C temperature.

T	Sample IDs	Rs $\Omega.cm2$	Rct K. $\Omega.cm2$	CPEFdl $\mu F/cm2$	ndl	Rf K. $\Omega.cm2$	CPEf $\mu F/cm2$	nf	Rt(Rct+Rf) K. $\Omega.cm2$	X2	%
25 C	W-316L	13.61	124.8	1.67E-04	1	122.1	6.51E-05	0.91	246.9	3.26E-04	
	ED30	13.5	97.24	3.24E-07	1.03E-02	280.4	5.57E-05	0.92	377.64	4.26E-04	53%
70 C	W-316L	2.73	6.67	-5.1E-04	0.380	-1.59E-02	1.1E-04	0.85	6.66	2.3E-02	
	ED33	-36.70	5.27	8.1E-04	0.761	2.146	6.2E-05	0.70	7.42	1.9E-03	11%

Figure 41 depicts the CPDP curves for the samples fabricated using SLM and wrought 316L. The CPDP test help in understanding the corrosion behavior of 3D-printed stainless steels. Table 13 summaries the data extracted from the CPDP curves using the Tafel slope in 3.5% NaCl solution at two temperature values.

The 3D printed sample of ED30T has higher E_{pit} values when compared to W-316L at room temperature. This gab is reduced when we increase the temperature to 70 C. On the other word, at room temperature, ED-30T has better corrosion resistance by 36 % than W-316, while at temperatures of 70 C, this gab of corrosion resistance is reduced to be only 20 %. Therefore, it is important to consider the operating temperature when selecting the appropriate material for a specific application, as the corrosion resistance of materials can vary significantly at higher temperatures. Additionally, other factors such as pH and chemical composition of the environment

should also be taken into account. The E_{corr} of ED-30T is moved to higher potentials than W-316 samples, indicating that they are less susceptible to corrosion. However, there is slight different of the corrosion potential (E_{corr}) between ED-30T and wrought 316L at temperature of 70 C.

It was mentioned earlier that the reason the SLMed sample exhibited excellent pitting corrosion resistance was that it did not have MnS inclusions, which were thought to be sensitive to pitting corrosion. [40]. Whereas, it was found that the main cause of pitting corrosion in SLMed 316L stainless steel was that it had pores [41]. However, the pitting resistance of SLMed 316L stainless steel can be improved by optimizing the processing parameters to reduce the porosity.

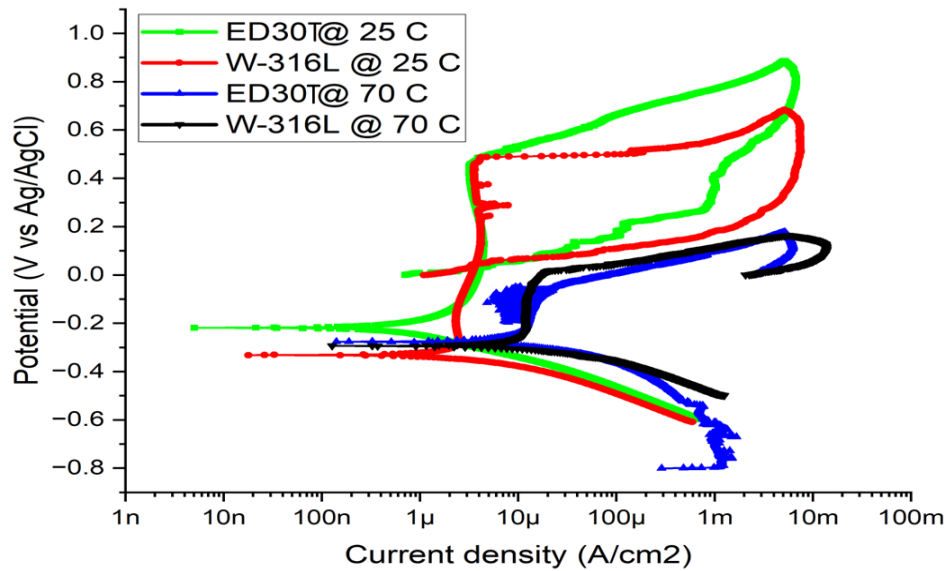


Figure 41: Cyclic potentiodynamic polarization curves at 3.5 % NaCl solution

Table 13: The results of Tafel fitting extract from CPDP curve at pH1for room temperature and 70 C temperatures.

T	Sample IDs	Beta A	Beta C	Icorr	Ecorr	CR	Eff %	I_{pit}	E_{pit}	E_{rep}	E_{pit}-E_{rep}
		mV/dec	mV/dec	μA/cm²	mV	mpy		μA	mV	mV	
25 C	W-316L	7.50E+14	0.08	2.13	-307	2.78	-	3.35	423.1	71.43	351.6
	ED30T	4.00E+14	0.22	1.35	-248.6	1.75	36%	3.93	494.5	60.95	433.55
70 C	W-316L	4.51	0.0584	4.28	-294	5.569		20.6	17.8	-137.9	155.77
	ED30T	1.00E+15	6.42E-02	3.418	-2.7E+02	4.451	20.16%	24.3	-46.5	-270.4	223.9

5.5 Corrosion behavior of long-duration immersed sample in Hydrocarbon and NaCl environments

The heat treated 316L SLMed (ED30T) stainless steel and the 316L wrought samples were immersed in 3.5% NaCl and crude oil (hydrocarbon) for 14 days at room temperature. In order to gain a better understanding of the 316L SLMed sample's corrosion behavior in a hydrocarbon environment and to compare it with its behavior in 3.5% NaCl. This will contribute to the development of more effective corrosion protection strategies for 316L SLMed stainless steel in hydrocarbon environments, which are commonly encountered in the oil and gas industry.

Table 14 shows the corrosion rate after immersion in a 3.5% NaCl solution and crude oil. In this study, it was found that the rate of corrosion of the sample that was exposed to 3.5% NaCl was much higher than that of the sample that was submerged in crude oil, which is unexpected because crude oil has more salts and other corrosive substances than 3.5% NaCl. This could be due to the fact that crude oil also has many components that can act as corrosion inhibitors and

slow down the corrosion process, or it could be due to the fact that the electrolyte amount and the conductivity of the crude oil are much lower than in the 3.5% NaCl solution [82].

Table 14: The calculated corrosion rates of SLMed and wrought samples after immersion test in 3.5% NaCl solution and crude oil for 14 days.

solution	Sample IDs	Calculated Corrosion rate
		mpy *10 ⁻²
3.5 NaCl, pH1	W-316L	7.97
	ED30	4.84
Crude oil, pH 1	W-316L	2.66
	ED30	1.56

In contrast, the corrosion rates of both ED30T and W-316L samples show a similar trend when tested with LPR results (Table 11) and immersion in a 3.5% NaCl solution at pH 1 (table 14). The corrosion rate that was calculated from the LPR result shows that the ED30T sample has a lower corrosion rate, which is also shown in the immersion test corrosion rate calculation. This could be proof that the ED30T sample is more resistant to corrosion than the W-316L sample in a 3.5% NaCL solution at pH 1. This could mean that ED30T and 3D printed material have a high potential to be used in corrosive environments and hydrocarbons.

Figure 42 shows the typical 3D profilometer images, 2D optical images, and line profiles showing the pit density and depth for W316L and ED-30T immersed at 3.5% NaCl and crude oil. Pitting

analysis was performed by using the profilometer software. Figure 43 shows the maximum pit depth, average pit depth, and pit density of W-316 and ED 30 after the immersion test in 3.5% NaCl and crude oil for 14 days. After being immersed in 3.5% NaCl and crude oil for 14 days, the pitting analysis showed that W316L and ED-30T had different levels of pit density and depth. Figure 44 provides a comprehensive overview of the maximum pit depth, average pit depth, pit density, and pit size for both materials under these conditions. It was observed that the samples immersed in crude had a higher pit density than the samples immersed in a 3.5% NaCl solution. However, the pit depth was found to be deeper in the samples immersed in a 3.5% NaCl solution compared to those immersed in crude oil. Furthermore, the samples that were exposed to crude oil had larger pit sizes. These findings indicate that the corrosive effects of crude oil may lead to a higher density of pits, while the 3.5% NaCl solution may cause deeper and larger pits on the tested materials. There is a proportional correlation between the pit density and the pit depth; when the pit density increases, the pit depth decreases. This indicates that the corrosive nature of the 3.5% NaCl solution may result in a higher concentration of pits, but these pits tend to be deeper compared to those caused by crude oil exposure, which are shallow. In addition, when the pit density increases, the pit size increases. This suggests that the corrosive nature of the crude oil not only increases the number of pits formed but also leads to larger but shallower pit sizes. Therefore, the type of corrosive medium plays a significant role in both the density and depth of pits formed on the tested materials.

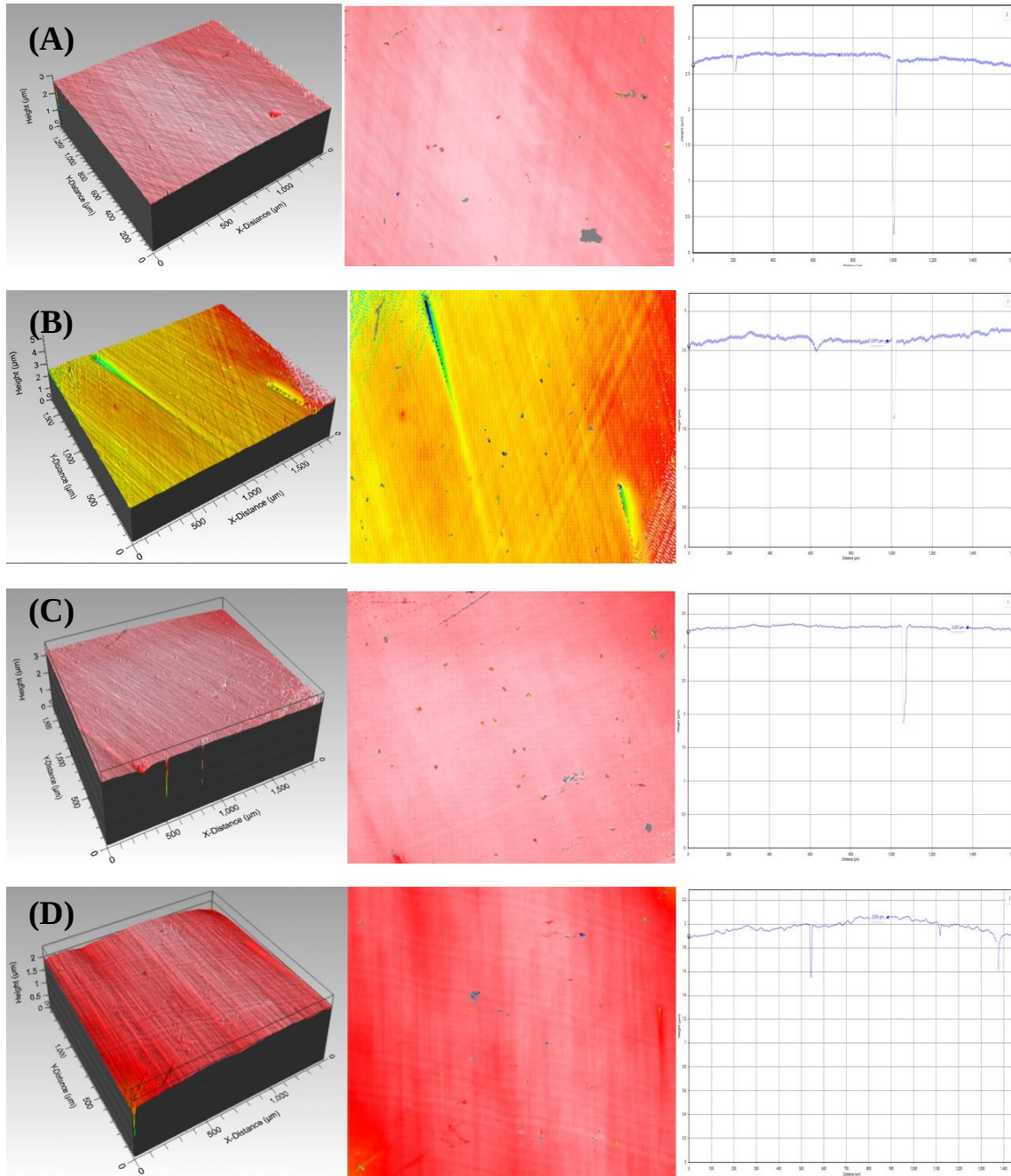


Figure 42: Typical 3D profilometer images, 2D optical images, and line profiles showing the pit density and depth for A) W316L at 3.5% NaCl, B) ED30 at 3.5% NaCl, C) W316L at crude oil, D) ED30 at crude oil.

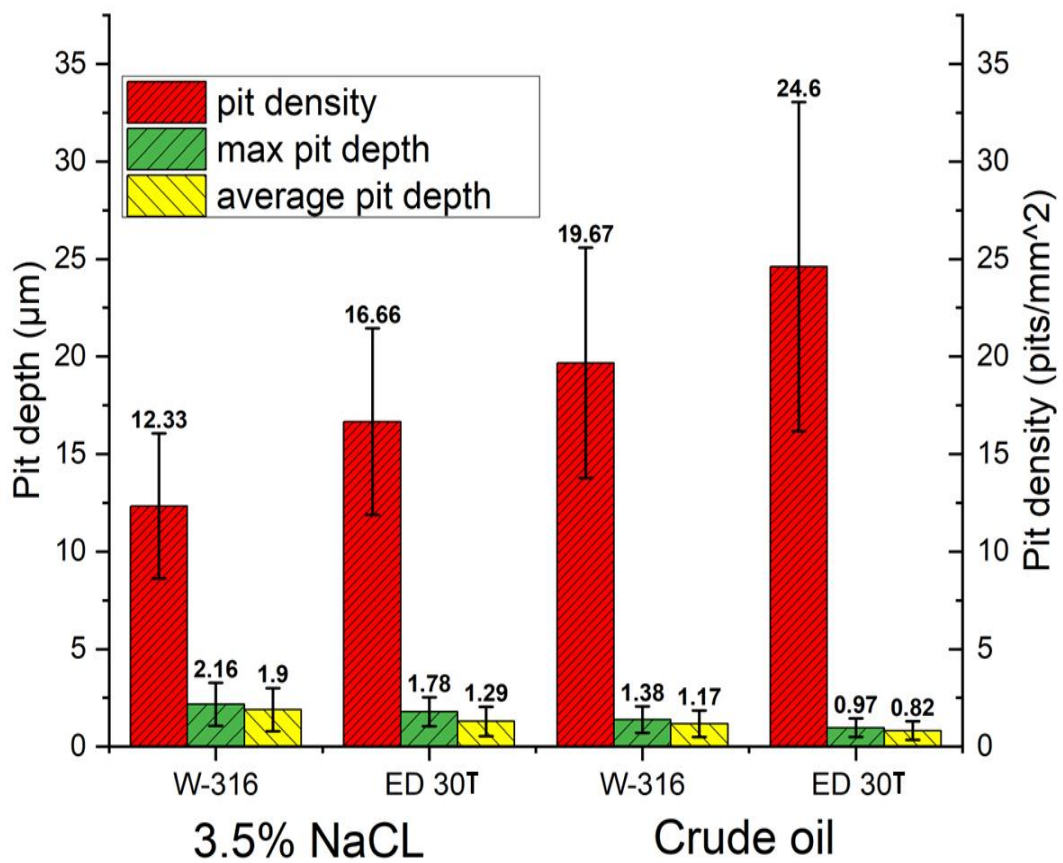


Figure 43: Max pit depth, average pit depth and pit density of W-316 and ED 30 in crude oil and 3.5% NaCl solution.

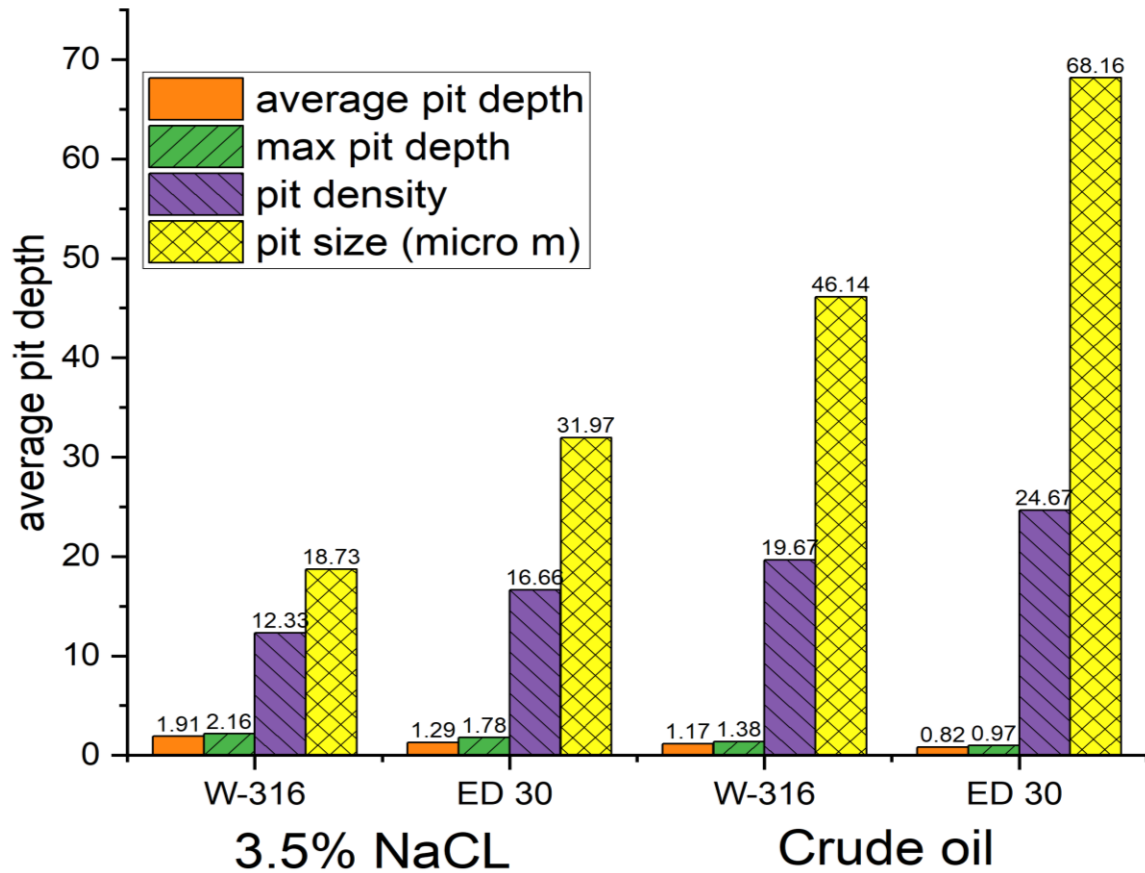


Figure 44: Average pit depth, max pit depth, pit size and pit density of W-316 and ED 30 in crude oil and 3.5% NaCl solution.

The findings indicate that pitting corrosion is less likely in a NaCl solution, whereas the number of pits increases in crude oil. However, the pit depth in 3.5% NaCl is 36 % deeper than that in crude oil. This is because of the formation of water in crude oil emulsions in stable conditions [83]. The water will not mix properly with the oil due to its density differentiation, which led to a huge number of droplets forming on the immersed specimen surface. Each droplet will cause a shallow pit on the sample surface, but over a huge area. For this reason, the pit density of both samples (ED-30T and W-316L) in the crude oil is greater than the pit density in the 3.5% NaCl solution.

Figure 47 shows the process for the formation of water-in-oil emulsions for more understanding for the above phenomena. The formation of water-in-oil emulsions occurs when water droplets become dispersed within the oil due to their inability to mix properly. This process is influenced by the density differentiation between the two substances. Figure 45 provides a visual representation of this phenomenon, aiding in a better understanding of the increased pit density observed on the sample surfaces immersed in crude oil compared to those in the 3.5% NaCl solution.

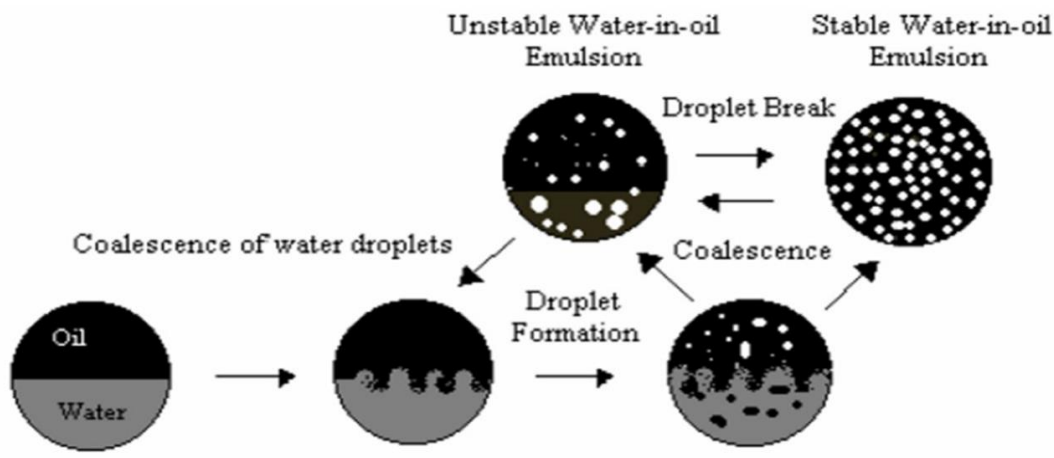


Figure 45: The process for the formation of water-in-oil emulsions [83].

Finally, the results of this study suggest that the corrosion behavior of 3D printed materials in oil and gas environments is complex and dependent on various factors. Therefore, further research is necessary to fully understand the mechanisms involved and develop effective corrosion prevention strategies.

CHAPTER 6 CONCLUSIONS

6.1 General Summary

In this study, SLM 316L stainless steel samples were fabricated using SLM with different energy densities and conventional wrought 316L samples were investigated for corrosion performance in a 3.5 wt. % sodium chloride solution at room temperature (constant) under different pH values and at high temperature. Also, immersion test was conducted in 3.5 wt. % sodium chloride solution and crude oil for 14 days. After performing the microstructure, pitting evaluation and electrochemical corrosion tests, the following conclusions can be drawn.

- The SLMed samples with low energy density (21 J/mm^3) show very low corrosion resistance due to its high porosity and high number of pores. The high porosity and high number of pores are a result of the unmelted metal powder and low input energy density. In this study, it was found that the main cause of pitting corrosion in SLMed 316L stainless steel was that it had pores. Corrosion behavior has been researched as a function of the key SLM parameters (laser power and scan speed), which significantly affect the material's pores. However, the SLMed 316L samples that have high energy density of 33 J/mm^3 show a better corrosion performance than 316L wrought samples in all pH levels. This indicates that selective laser melting (SLM) process has a positive impact on the corrosion resistance of 316L stainless steel, making it a promising technique for fabricating corrosion-resistant parts.
- For both 316L SLMed samples and 316L samples, the pH has a significant effect

on their corrosion behavior. Under the same pH conditions, the corrosion rate of 316L SLMed samples is lower than that of 316L wrought samples. This suggests that selective laser melting can improve the corrosion resistance of 316L stainless steel.

However, they had the same trend when the pH level was decreased, the corrosion rate increased.

- Increasing the temperature of a 3.5% NaCl solution has a negative effect on the corrosion rate and pitting corrosion. When the temperature increased, the pitting potential decreased, which lowered the material's resistance to pitting corrosion. This is because higher temperatures increase the rate of chemical reactions, which can lead to more rapid corrosion and pitting.
- The pitting resistance of the SLM-316L stainless steel (ED30T) was found to be higher than that of the wrought alloy, especially at pH 1, where the E_{pit} values of the samples show a clear difference. Other corrosion properties, like corrosion rate and corrosion potential, didn't change much between the samples.
- It was detected in this study that when the percentage of porosity increased, the re-passivation potential decreased, such as in ED-20, which has the lowest re-passivation value. However the SLM samples have a higher passivity film thickness than wrought samples based on calculation and EIS data, but the difference is not significant.
- The SLMed 316L sample has better corrosion resistance at high temperatures than wrought sample.

- In crude oil, the corrosion resistance of SLMed 316L was greater than in the 3.5% NaCl solution. This suggests that SLMed 316L could be a promising material for oil and gas pipelines and other oil and gas industry environments. Further research could explore its potential for long-term durability and performance.

6.2 Recommendations for future work:

Additive manufacturing, or 3D printing, of the SLMed stainless steel has a promising future in the oil and gas industries and can be used instead of stainless steel materials manufactured with conventional methods. More future optimization shall be conducted for the SLM process parameters to have high quality fabricated SLMed metal and low porosity. Below are some of the suggested fields to work on:

- Study the effect of the heat treatment on the SLM sample, even with its high porosity. On the other words, can the heat treatment for the SLMed metal increase the relative density of the fabricated metal and reduce its porosity? The heat treatment can potentially improve the mechanical properties of the SLM sample, such as its strength and ductility. However, it is important to carefully control the temperature and duration of the heat treatment to avoid introducing new defects or causing excessive grain growth.
- Study the SLMed metal samples in an alkaline environment (pH range: 7 to 14). Is it more corrosion resistant, such as in an acidic environment, or will the trend change? The study of SLMed metal samples in an alkaline environment is important to understand their corrosion resistance in a wider pH range. This knowledge can be useful for various applications where the metal will be exposed to different pH levels, such as in wastewater

treatment plants or chemical processing industries.

- More attention needs to be put on the weldability of the SLMed material and its effect on the microstructure and corrosion behavior. This is particularly important in industries such as aerospace and oil and gas, where the quality and reliability of the material are critical for safety and performance. Further research on this topic can lead to improvements in the design and manufacturing of SLMed components.
- Study 3 D printed materials in high temperature hydrocarbon environment. This study is important for understanding the potential applications of 3D printing in industries that require materials to withstand high temperatures and harsh environments. The findings could lead to the development of new materials that are more durable and efficient in these conditions.

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VITAE

Name: Ibrahim Awad Albalawi

Nationality: Saudi Arabia

Date of Birth: 08 Dec, 1989, Alkhobar , Saudi Arabia

Email: Ibrahim.a.albalawi@gmail.com

Current Address: Al Shoualah – 4077 Dammam, Saudi Arabia, Zip Code: 34261

Academic Background: Completed BS Degree in Mechanical Engineering from Ferris State University, Michigan State, USA in May 2017

Professional: Material engineer at Wood Group consulting, 2017 - 2018
Inspection and Corrosion Engineer at Saudi Aramco Total refinery and petrochemical company (SATORP) 2018 - present