

**[CORROSION OF STELLITE-6 OVERLAY CLADDING ON
304L STAINLESS STEEL IN NITRIC ACID]**

BY

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*This Study is dedicated to my family who have been the source inspiration and strength.
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ABSTRACT

Full Name : [Omar Mohammed Alsadoon]
Thesis Title : [Studying the Corrosion of Stellite-6 overlay cladding on 304L stainless steel in nitric acid and investigating the heat treatment process on lowering the Stellite-6 overlay corrosion resistance]
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Stellite-6 alloy (ST6) is widely used as an overlay coating to protect substrates from wear, erosion and corrosion. In nitric acid (HNO_3) environments, the interface zone between the overlay and the substrate alloys usually suffers from corrosion attack. Internal gate valve parts corrode in nitric acid production facilities and their failures cause a significant financial impact. This study investigates the corrosion of gate valves constructed of 304L stainless steel fabricated using gas tungsten arc welding in HNO_3 . Three zones—the Stellite-6 overlay, 304L stainless steel, and the zone at the interface between the Stellite-6 overlay and 304L stainless steel—were represented by samples from the valve gate. The findings demonstrated inter-dendritic corrosion and homogenous corrosion attacking the interface zone. The corrosion rates of these three zones were determined using linear polarization resistance method in 40% HNO_3 at 25 C. Due to the diluting effect, the interface zone among the three zones showed the highest corrosion rate. The interface zone's chromium content was lower than that of the Stellite-6 alloy, which resulted in a lower level of corrosion resistance. Additionally, the zero-resistance ammeter method was used to study the galvanic corrosion of the interface zone. With respect to Stellite-6, the interface zone exhibited galvanic corrosion and acted as an anode. On the other hand, its behavior in relation to 304L was discovered to be cathodic. The diluting effect, which led to the development of a chromium concentration gradient between the interface zone and the Stellite-6 bulk alloy, was likewise connected to the galvanic corrosion of the interface zone. Dendrites developed during the Stellite-6 overlay welding process, which produced chemical composition inhomogeneity and accelerated inter-dendritic corrosion. In the inter-dendritic areas, precipitation of chromium carbide was also noticed. These

precipitates reduced the dendrites' peripheries' corrosion resistance by causing chromium depletion. In addition, several heat treatment regimens were investigated in this work for the purpose of studying the effect of heat treatment on the ST6's corrosion resistance in nitric acid environment. The changes in the microstructure morphology were studied using SEM, EDS and XRD. The corrosion rates were measured using Electrochemical Corrosion analysis among the studied specimens. Hardness measurement was performed to ensure that no heat treatment regime would cause an undesirable loss of the specified alloy's standard hardness. It was found that heat treatment under 1200 °C for 2 hours produces a homogeneous microstructure and low level of dilution resulting in low corrosion rates compared with the as-welded and the other specimens that were heat treated under different temperatures. On the other hand, heat treatment, under 950 °C and 800 °C for 2 hours was not able to produce a homogeneous microstructure and caused the specimens to undergo high corrosion rates although the level of dilution noticeably lowered.

ملخص الرسالة

الاسم الكامل: عمر محمد السعدون

عنوان الرسالة: دراسة ظاهرة التآكل في السبائك المطلية بمادة ستيليت-6 (Stellite-6) ودراسة تأثير أنظمة المعالجة الحرارية للسبائك على خفض معدلات التآكل

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تاريخ الدرجة العلمية: ديسمبر 2023

تُستخدم سبائك الستالايت (ST6-6) على نطاق واسع كطلاء لحماية المعادن المطلية من أثر التعرية الناتجة عن احتكاك المعادن (erosion) أو التآكل (corrosion). في بيئات تحتوي على حمض النيتريك، عادةً ما تعاني السبائك المطلية من تهديد التآكل وخصوصاً في المنطقة الفاصلة بين السبيكة وطلائها. على سبيل المثال، تتآكل هذه الأجزاء في الصمامات عند تعرضها لحمض النيتريك (HNO_3) في مرافق تصنيع هذا الحامض مما يؤدي إلى خسائر مادية تترتب على صيانة أو تغيير الصمامات المصابة. تستخدم هذه الدراسة عينات مأخوذة من صمامات مصابة بالتآكل نتيجة لتعرضها إلى HNO_3 . وجدير بالذكر أن الصمامات مصنوعة من الفولاذ المقاوم للصدأ (Stainless Steel 304L) طليت بمادة الستالايت (ST-6) اللحام القوسي التنغستن (GTAW). تم تمثيل ثلاث أجزاء في جسم الصمام للدراسة وهي منطقة تحتوي على مادة الصمام الأصلية والطلاء المنطقة الموجودة في الواجهة بين ستالايت 6 والفولاذ المقاوم للصدأ 304. أظهرت النتائج تآكلاً شجيراً وتآكلاً متجانساً يهاجم منطقة الواجهة. تم تحديد معدلات التآكل لهذه المناطق الثلاث بمساعدة طريقة مقاومة الاستقطاب الخطي (Linear Polarization Resistance) في 40% HNO_3 عند 25 درجة مئوية. أظهرت منطقة الواجهة بين المناطق الثلاثة أعلى معدل تآكل. كان محتوى الكروم في منطقة الواجهة أقل من محتوى سبيكة Stellite-6، مما أدى إلى انخفاض مستوى مقاومة التآكل. بالإضافة إلى ذلك، تم استخدام طريقة مقياس المقاومة الصفرية (Ammeter Resistance Zero) لدراسة التآكل الجلفاني لمنطقة الواجهة. فيما يتعلق (ST-6)، أظهرت منطقة الواجهة تآكلاً جلفانياً وعملت هذه المنطقة من الصمام كأنود. ومن ناحية أخرى، تم اكتشاف أن سلوكها فيما يتعلق بـ (Stainless Steel 304L) كان كاثودياً. تطورت التشعبات أثناء عملية اللحام المتراكب Stlat-6، والتي أنتجت عدم تجانس التركيب الكيميائي وتآكل شجري متسارع. في المناطق المتداخلة، لوحظ أيضاً ترسيب كربيد الكروم. قللت هذه الرواسب مقاومة التآكل في أطراف التشعبات من خلال التسبب في استنفاد الكروم هناك. بالإضافة إلى ذلك، تم التحقيق في العديد من أنظمة المعالجة الحرارية في هذا العمل لغرض دراسة تأثير أنظمة المعالجة الحرارية هذه على مقاومة التآكل لـ ST6 في بيئة حمض النيتريك. تمت دراسة تأثير المعالجة الحرارية

من خلال التحقق من التغير في مورفولوجيا البنية المجهرية (تحليل SEM / EDS و XRD) وأيضاً عن طريق التحقق من معدلات التآكل (تحليل التآكل الكهروكيميائي) بين العينات المدروسة. تم إجراء قياس الصلابة للتأكد من أن أي نظام معالجة حراري مستخدم سوف لن يتسبب في تأثير غير مرغوب فيه للصلابة القياسية للسبائك المحددة. وجد أن المعالجة الحرارية تحت 1200 درجة مئوية لمدة ساعتين تنتج بنية مجهرية متجانسة مما يؤدي إلى معدلات تآكل منخفضة مقارنة بالعيينة الملحومة والعيينة الأخرى التي تمت معالجتها حرارياً تحت درجات حرارة مختلفة. من ناحية أخرى ، لم تتمكن المعالجة الحرارية تحت 950 درجة مئوية و 800 درجة مئوية لمدة ساعتين من إنتاج بنية مجهرية متجانسة وتسببت في تعرض العينات لمعدلات تآكل عالية.

CHAPTER 1

INTRODUCTION

In industries that produce nitric acid (HNO_3), austenitic stainless steels are used for a variety of components, including pressure vessels, pipelines, and valves. Certain grades of stainless steel, such as 304 and 304L, function admirably over a wide temperature and HNO_3 concentration range. Their corrosion rates at low temperatures at HNO_3 concentrations ranging from 0 to 90% do not exceed 0.13 mm/y [1]. In addition, their corrosion rates remain moderate even at temperatures above the boiling point of HNO_3 so long as HNO_3 concentrations are maintained below 50% [1]. Due to their resistance to corrosion, these materials are typically used for the management and storage of HNO_3 at various temperatures and concentrations [1].

The gate valve is a common type of valves used in HNO_3 production facilities. Typically, these valves are usually used where the process stream is required to be either in flow mode (valve is fully opened) or blocked condition (valve is fully closed). As Figure 1.1 illustrates, gate valves consist of a body and a bonnet that encapsulate the valve internals namely the gate of the valve, the stem and the gate seat. The valve stem is physically connected to the gate, and when the valve is in a closed position, the gate bottom end subsides on the gate seat lower portion blocking the flow between the valve inlet and outlet. When the hand

well is rotated, the gate rises along with the stem allowing the flow to pass by which the gate slides through the gate seats.

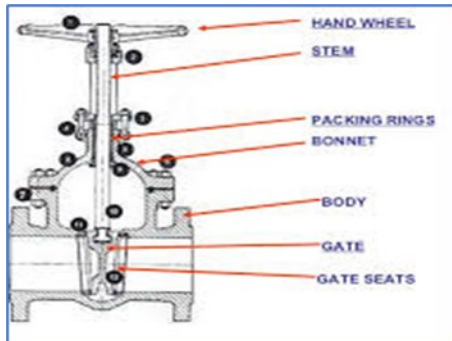


Figure 1-1: Gate Valve Assembly

As the internal components of valves (gates, disks, guides, and seats) are exhibited metal-on-metal sliding contacts, they are susceptible to wear. As depicted in Figure 1.2, it is practical to apply high wear resistant coating such as Stellite-type overlay alloys to the interior components of the valves to prevent the valve's internal from threats associated with wear attack. Stellite-6, a cobalt-chromium-based alloy with superior wear and corrosion resistance [2] is the most prevalent overlay alloy for these applications.

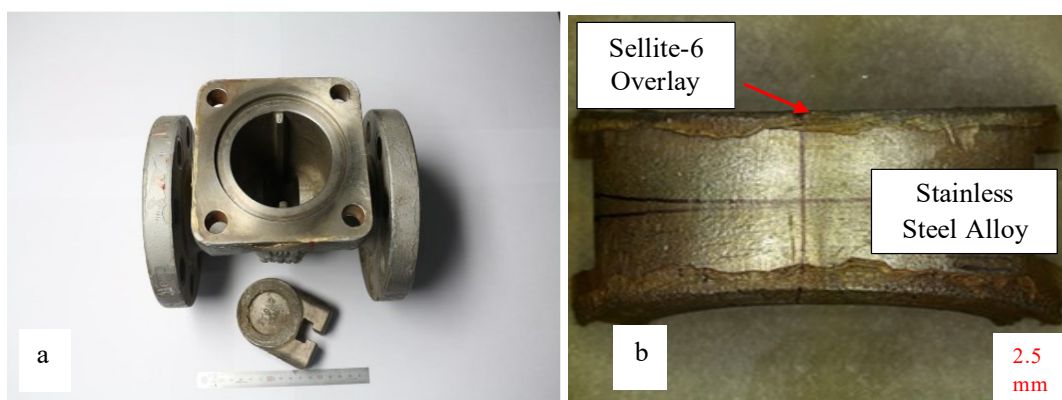


Figure 1-2: Gate valve type assembly; (a) valve body and (b) the valve gate part

In fact, users of these valves intentionally limit the cladding to the surface of the valve's internal parts that are exposed to the risk of wear. As an example, overlying the gate part

of a valve is usually applied to the gate faces only because they represent the area of contact with the gate seats.

Thus, partial gate cladding will result in forming an interface zone between the cladding overlay alloys and the gate substrate material that has not been cladded. Consequently, the interface area as shown in Figure 1.3 will involve two discrete heat affected zones (HAZ), namely, the heat affected zone of the Stellite-6 overlay (HAZ-1) and the heat affected zone of the stainless steel substrate (HAZ-2). In operation, the valve gates suffer from a corrosion attack (Fig. 1.4). A separation (decohesion) of the overlay layer from the substrate is brought on by the corrosion of HAZ-1 (on the Stellite-6 alloy region) in the interface zone. This decohesion appears to split the two connected alloys over their fusion line. Additionally, it is evident that HAZ1 corrosion started at the valve gate's exterior surface and spread laterally. While the stainless steel mating surface (HAZ-2) showed little to no metal loss, HAZ-1 underwent extensive corrosion. Figure 1.4b depicts inter-dendritic corrosion caused by HAZ-1 under high magnification optical examination. Stellite-6 dendrites are separated from the main alloy's matrix. These findings imply that HAZ-1 experiences two different forms of corrosion: uniform corrosion, which results in substrate-overlay decohesion; and localized (inter-dendritic) corrosion, which is brought on by a full dendrite.

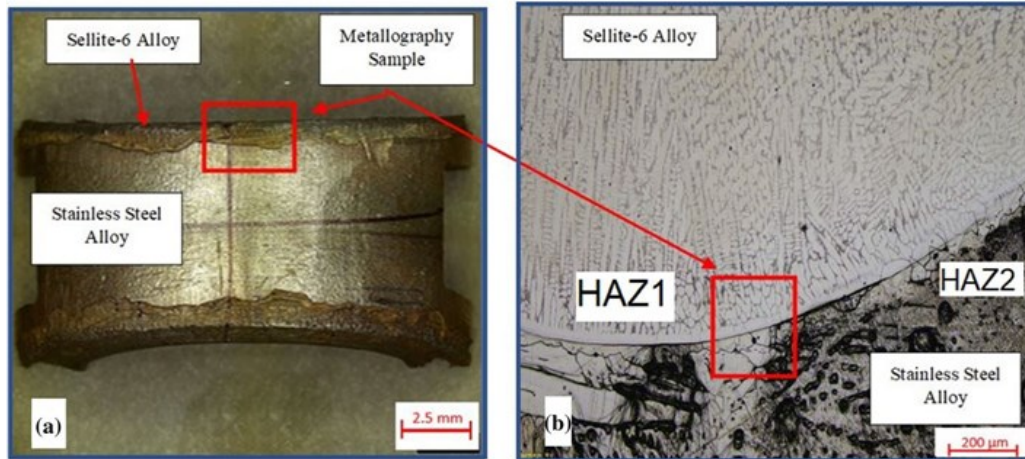


Figure 1-3:(a) Photograph image of the valve gate showing Stellite6 overlay cladding on 304L stainless steel, (b) optical micrograph of the welding interface showing HAZ1 and HAZ2

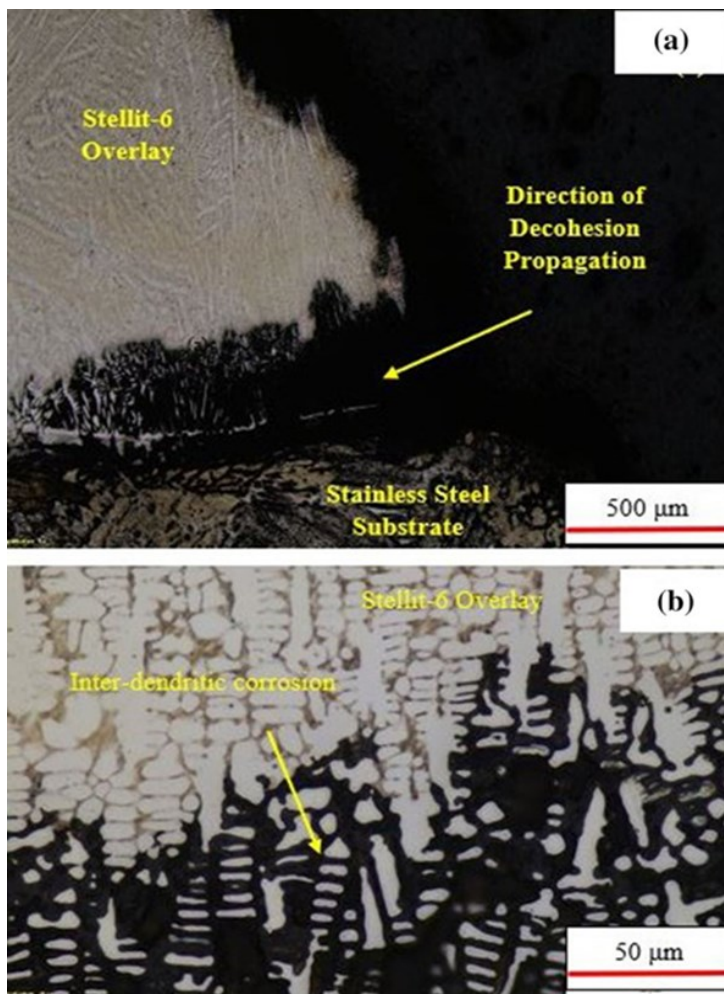


Figure 1-4: Optical micrograph of the corroded sample showing decohesion between the stainless steel and Stellite-6 overlay propagation initiation site

The mechanical properties and corrosion resistance of Stellite alloys depend not only on their chemical composition, but also on the overlying deposition procedure (welding/casting process) [3]. Using different welding processes or altering the welding parameters of a specific welding process during Stellite overlaying results in a different microstructure and chemical composition of the overlay alloy [3]. Therefore, the interface region between the clad and substrate alloys will contain zones with distinct microstructures and chemical compositions. Literature attributes the chemical composition variation between these zones to the dilution effect [4] and the precipitation of coarse chromium carbides [5] within the microstructure of the overlying alloy.

It is widely believed that Stellite provides corrosion, cavitation, and erosion resistance [2], despite the fact that it is typically prescribed for high-temperature mechanical wear resistance. Stellite corrosion resistance, however, can be negatively impacted by microstructural and chemical composition changes. In petrochemical and chemical industries, such as nitric acid production plants, Stellite-6-clad 304L stainless steel valves have been documented to be subject to severe corrosion attacks in environments containing nitric acid. The attack occurs in the gate of these valves, resulting in failure to close properly. As a consequence of the failures, these valves cannot perform their intended function, resulting in significant maintenance costs and production losses in these industries.

In this particular alloy combination (Stellite-6/304L stainless steel), the gate parts of these valves were attacked by localized corrosion in the interfacial zone between the clad and the substrate alloy. Observations indicate that the clad alloy exhibits greater corrosion deterioration than the substrate alloys. This observation has led to the belief that the

corrosion attack associated with the Stellite-6/304L stainless steel cladding system is primarily attributable to the difference in the corrosion resistance of the different zones involved in this cladding/substrate system. Therefore, this study aimed to investigate the corrosion mechanism of the various zones formed by cladding 304L stainless steel with Stellite-6 in 40% nitric acid at 25 °C. Additionally, the galvanic behavior of zones with distinct microstructural and chemical compositions will be investigated. In addition, the work will examine the effect of a particular heat treatment regime on the corrosion resistance of these alloy combinations. |

CHAPTER 2

BACKGROUND

This section provides a general overview of Stellite alloys and characterize the corrosion resistance of Stellite-6 in particular. The factors influencing the corrosion resistance of Stellite-6 is discussed. Controls of these influencing factors is also investigated.

2.1 Stellite Alloys Overview

Historically, two distinct compositional families of commercial cobalt-base alloys were developed: Co-Cr-W and Co-Mo. Elwood Hynes was one of the first researchers to investigate the high strength and non-staining properties of these alloys in the early 20th century. He emphasized the importance of tungsten and molybdenum in imparting strength to cobalt-based alloys. Due to their lustrous appearance, Hynes named these alloys Stellite, which is derived from the Latin word Stella, which means star [6].

Worth noting that Hynes' research that highlighted and shed light on the high strength of Stellite alloys has resulted in the increased use of these alloys as cutting tools. However, after the First World War in 1922, the use of Stellite alloys was expanded to include wear-resistant coatings for industrial component surfaces. Since that time, Stellite technology has been employed as a hardening agent in a variety of mechanical applications, including plowshares, oil well drilling tools, dredging cutters, hot trimming dies, and internal combustion engine valves and valve seats [6].

In hard-facing applications, Stellite on a substrate can be achieved by the most common welding process. Melting the overlay alloys followed by casting them on the substrate

material is also used to a certain extent in the industry. In both processes, a filler metal of the Stellite alloy is melted and deposited on the substrate surface.

In its terminology, the term Stellite is followed by a numeral or an alphabetic letter, such as 1, 6, 12, or F, to indicate the alloy's fundamental properties, such as its chemical composition and hardness. Table-2.1 lists the chemical composition of several Stellite alloys.

Table 2-1" Chemical Composition of Stellite alloys [2]

ALLOY	NOMINAL ANALYSIS OF WELDING ROD								Others	Hardness (HRC)
	Co	Cr	W	C	Ni	Mo	Fe	Si		
Stellite-1	Bal.	32	12	2.45	<3.0	<1.0	<3.0	<2.0	<0.5	51–56
Stellite-6	Bal.	30	4–5	1.2	<3.0	<1.0	<3.0	<2.0	<0.5	40–45
Stellite-12	Bal.	30	8	1.55	<3.0	<1.0	<3.0	<2.0	<0.5	46–51
Stellite-20	Bal.	33	16	2.45	<3.0	<1.0	<3.0	<2.0	<0.5	53–59
Stellite-21	Bal.	28	—	0.25	3	5.2	<3.0	<1.5	<0.5	28–40
Stellite-25	Bal.	20	14	0.1	10	<1.0	<3.0	<1.0	<0.5	20–45
Stellite- F	Bal.	26	12	1.7	22	<1.0	<3.0	<2.0	<0.5	40–45
Stellite-706	Bal.	31	—	1.2	<3.0	4	<3.0	<1.0	<1.0	39–44
Stellite-712	Bal.	31	—	1.55	<3.0	8	<3.0	<2.0	<1.0	46–51

Stellite alloys with lower carbon contents, as Stellite-21 or Stellite-25, offer higher cavitation and slide wear resistance. However, they are known with moderately lower erosion resistance [2]. On the other hand, high carbon alloys like Stellite-1 and 20 are typically chosen for extreme abrasion wear and erosion situations [2]. Stellite-6 is regarded as the most widely utilized alloy used in different industrial applications because it demonstrates a compromise of these qualities [2].

In general, Stellite alloys contain tungsten, chromium, and molybdenum. To increase the production of chromium and other metal inter-dendritic carbides, which support excessive hardness, carbon is also added in specific proportions [7]. In high-temperature applications, chromium also interacts with the ambient oxygen to generate a protective oxide film, which enhances the corrosion resistance of the overlay alloy [7]. Sets of complicated carbides that are hindered in a matrix of solute Co-Cr solid solution typically make up its microstructure. When carbon is combined with additional elements like chromium, tungsten, nickel, and/or iron, carbides like M_7C_3 , $M_{23}C_6$, MC, and M_6C preferentially precipitate during the overlay process. As a result, the existing carbides give the overall alloy hardness, which increases the alloy's resistance to wear. In addition to the carbides, molybdenum and tungsten cause the formation of intermetallic compounds such $Co_3(Mo, W)$, which also aid in the rise in alloy hardness [8].

2.2 Stellite Alloys Corrosion Resistance

In oxidizing acid conditions, cobalt has lower corrosion resistance than nickel. Cobalt demonstrated a value of critical current in 1 N H_2SO_4 that was 14 times higher than the critical current of nickel, despite their passivity ranges being almost identical [6]. This fact raises a serious red flag about the use of cobalt-base alloys in corrosive, oxidizing conditions. Chromium is the key component in chromium-based overlay alloys' corrosion resistance in oxidizing settings, as noted in various publications [6].

The capacity of chromium to generate chromium-rich oxide coatings that shield the protected alloy from its corrosive environment is key to its ability to withstand oxidizing effects [9]. Numerous research conducted over the past few decades have shown that chromium oxide layer is highly successful in minimizing the negative effects of the

majority of oxidizing conditions. As a result, chromium is always able to create a stable, nonporous, and well-adhered oxide film. In fact, these characteristics are thought to be what gives chromium oxide film the benefits it has in terms of corrosion resistance [9].

Cobalt base alloys with a high chromium content, such as alloy 6B, showed a noteworthy corrosion rate in concentrated nitric acid, whereas alloys with low chromium content, such as alloys 188 and 25, showed minimal corrosion rates. According to Table 2.2's chemical breakdown of these alloys, alloy 6B has a higher carbon content than the other two alloys. That is, because carbon has caused the development of chromium carbide and sensitized the alloy, carbon enrichment has made alloy 6B less able to withstand oxidation corrosion [6].

Table 2-2: Chemical Composition of Cobalt base alloys [14]

Alloy	Chemical Composition %								
	Co	Cr	W	Mo	C	Fe	Ni	Si	Mn
6B	55.9	30	4	1.5	1	3	2.5	0.7	1.4
188	50	20	15	-	0.1	3	10	0.4	1.5
25	37.3	22	14	-	0.1	3	22	0.35	1.25

Thus, the presence of chromium gives overlay cladding alloys their resilience to corrosive oxidizing conditions. Despite being advantageous in creating carbides to raise the hardness of the cladding overlay, carbon increase unintentionally decreases chromium's ability to resist oxidizing corrosion due to the sensitization effect [6].

2.3 Factors Affecting Stellite Alloys Corrosion Resistance

As discussed in Section 2., the corrosion behavior and mechanical properties of Stellite alloys and Stellite-6 are coherently dependent on the variation in chemical composition and microstructure developed in the interface zone between the overlay and substrate. This

variation in chemical composition in the interface zone is primarily the result of dilution, it was also observed in the course of that discussion.

However, variations in chemical composition can also result from the nucleation and development of the dendritic microstructure during casting or welding [10]. The subsequent sub-sections discuss the variation in chemical composition caused by dilution and the formation of dendritic microstructures. Then, control measures for this variation in composition will be discussed.

2.3.1 Dilution

Atomic diffusion (migration) resulting from welding or casting procedures during overlaying causes dilution [4]. Due to this diffusion, the interface zone between the cladding and substrate alloys exhibits an elemental composition variation that affects both the cladding alloy and the substrate alloy. As shown in Figure 2.1, the atomic migration direction of a specific element is primarily determined by the concentration levels of that element in the two alloys in intimate contact. Thus, the element diffuses from sites with high concentrations to those with lower concentrations. For instance, in the combination of Colmonoy-6 overlay (73.5% Ni, 13.56% Cr, 4.75% Fe, and 4.23% Si) and 316LN substrate alloy (10 Ni, 16 Cr, 70 Fe, and 0.75 Si), nickel and silicon migrate from the Colmonoy-6 overlay into the 316LN substrate alloy due to the high concentrations of these elements in the Colmonoy-6 overlay relative to their concentrations in the 316LN substrate alloy. Chromium and iron, on the other hand, diffuse from the Colmonoy-6 overlay to the 316LN [4].

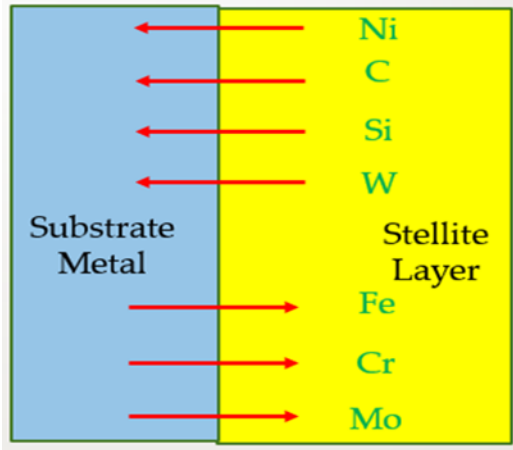


Figure 2-1: Elemental diffusion direction due to dilution

As shown in Figure 2.2 [11], dilution can be expressed as a percentage of the ratio of the area of penetration to the entire bead weld area. Using this geometry, the percentage of dilution can be calculated as:

$$Dilution(\%) = \frac{A_p}{A_p + A_r} \times 100 \quad (2.1)$$

Where A_p and A_r represent the bead penetration area and cross-sectional area of the reinforcement, respectively. In Equation (2.1), A_p represents the zone of substrate material that has melted and been mixed with infill metal. Therefore, if adequate mixing in the liquid is achieved, there can be no compositional gradient in the weld deposit [12]. This restricts the application of Equation (2.1) to situations where the concentration gradient associated with dilution is negligible. This limitation stems from the fact that Equation (2.1) was developed based on the assumption that there is no evaporation of the liquids during welding. However, evaporation always coexists with welding, reducing the concentration of certain elemental species [12]. In addition, a number of studies have demonstrated that welding dissimilar metals results in compositional gradients in the vicinity of the fusion line that can extend to a hundred microns [12].

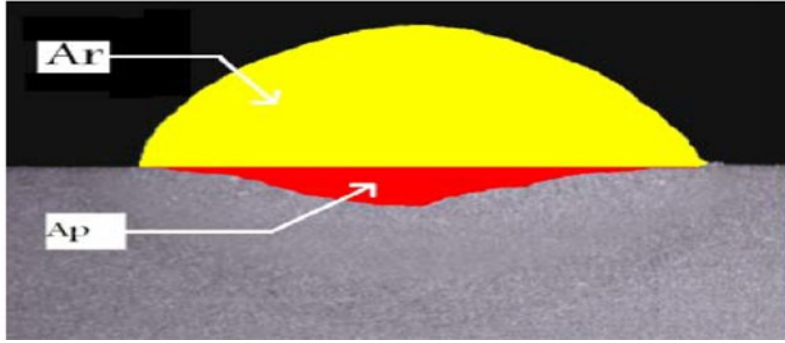


Figure 2-2: Dilution area penetration [12]

2.3.1.1 Factors Affecting Dilution

Whether dilution levels increase or diminish depends on a number of factors. These variables include the method chosen for applying the Stellite overlay alloys, either by welding or casting, as described in Section 2.1.2. Changing the deposition method's parameters also has a significant effect on dilution levels.

Using welding as an example of a deposition technique, researchers discovered that wire feed rate, welding voltage, nozzle-to-plate distance, welding speed, and gas flow rate have a significant impact on dilution [11]. Experimentally, it was determined that the dilution increases as the wire supply rate and welding voltage increase but decreases as the weld speed and nozzle-to-plate distance increase [11].

2.3.1.2 Dilution Effect on Corrosion Resistance

Chromium migrates from the Stellite-6 overlay to the 304L stainless steel substrate due to dilution, as demonstrated in Figure 2.3 for the assembly configuration of the Stellite-6-covered 304L stainless steel substrate. Thus, the chromium concentration gradient will follow the path A-B depicted in Figure 2.3, with a relatively steep gradient slope in a confined area (the interface zone). This area represents both the Stellite-6 overlay (HAZ-

1) and the stainless steel substrate (HAZ-2). In the presence of an electrolyte, the sharp slope of the chromium concentration gradient will result in a chromium concentration differential that can contribute to the formation of galvanic potential between (HAZ-1) and the bulk matrix of the Stellite-6 overlay.

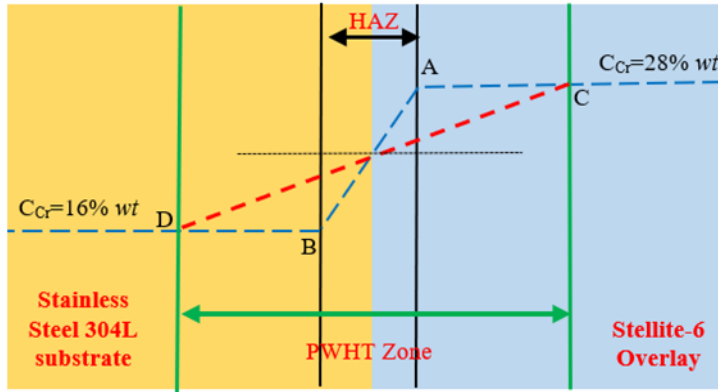


Figure 2-3: Chromium chemical composition gradient between stellite-6 and 306L substrate

2.3.1.3 Dilution Control

Due to the fact that dilution is a diffusion-related process, certain controls can be used to reduce the level of dilution. According to Fick's second law for non-steady state interdiffusion, the concentration gradient of a diffusible element is dependent on diffusion temperature, time, and distance.

$$\frac{C_s - C_x}{C_s - C_o} = \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (2.2)$$

C_s : Concentration of a diffusing element at the surface

C_o : Initial uniform concentration of element in alloy

x : Distance from surface

D : Diffusivity of diffusing solute element

t :Diffusion time

erf :Mathematical function called error function

According to Equation (2.2), the concentration differential of a diffusible element can be controlled by selecting diffusion parameters that generate a concentration gradient with a low slope. In other words, an application of heat treatment following Stillite-6 welding can be manipulated to accomplish the goal of lowering the chromium concentration differential in the interface zone. One way to accomplish this is to extend the heat treatment zone beyond the original HAZ, causing chromium diffusion during heat treatment to occur on a larger space bounded by the two green lines in Figure 2.3, large x -value in Equation (2.2). Thus, migration of chromium is forced to pursue the path C-D. Thus, the interface zone will benefit from a smaller chromium concentration gradient. In addition, optimizing the thermal treatment temperature and duration can further reduce the chromium concentration differential.

2.3.2 Dendrite Formation

During solidifications of a melt, the temperature of some locations falls below the liquidus temperature preceding the melt as a whole. At these locations, a solid particle becomes the nucleus of a newly crystallizing phase. The alloy concentration gradient surrounding the nucleus and the temperature gradient will then govern the growth of this crystal phase nucleus [10]. The crystal grows initially as a needle in the cretin-favored direction (thermal gradient direction), and subsequent growth of other nuclei leads to the formation of a forest of these crystals [10]. Secondary temperature gradients and melt segregation exist between parallel crystal needles, leading to the formation of dendritic microstructure [10] as depicted in Figure 2.4. When the lateral crystal reaches a certain width, voids form at the

edges of these secondary branches due to a dearth of adjacent liquid to supply the crystal [10].

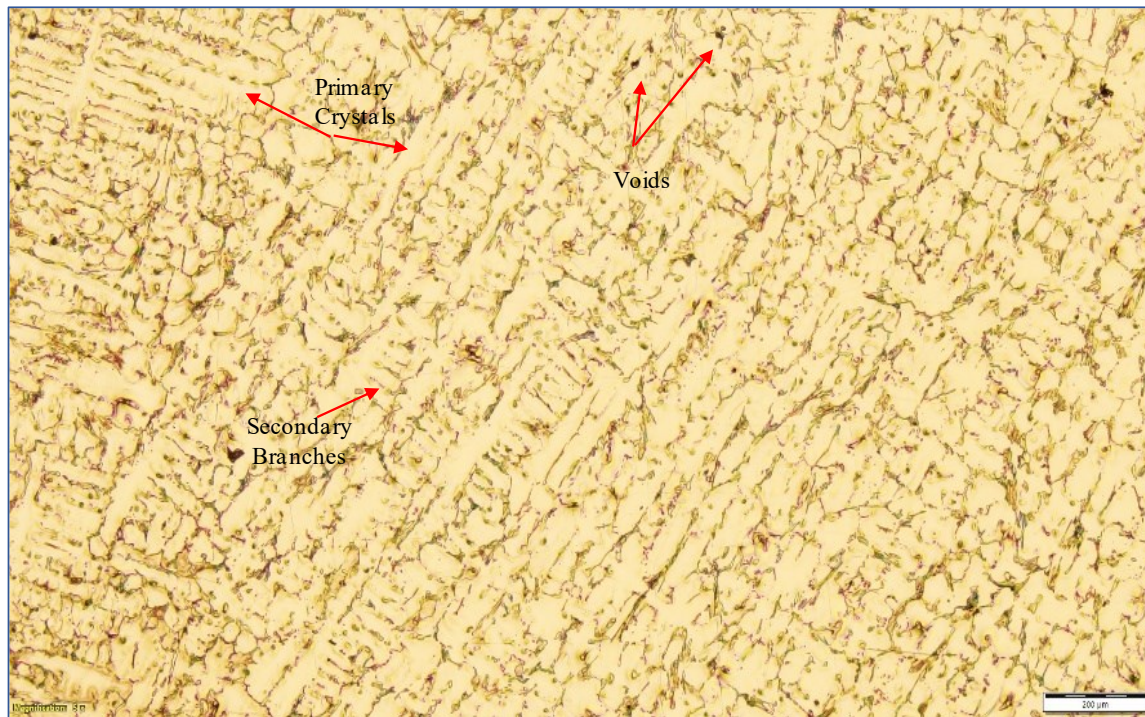


Figure 2-4: Dendritic microstructure of Ni-Cr superalloy

Concentrating on a single crystal during its growth phase reveals that the chemical composition of that crystal varies from its center to its periphery. As shown in region A of Figure 2.5, when the nucleus of a crystal is formed, adjacent liquid will deposit on it and solidify, producing the crystal's core. Until the final size of the crystal is fixed, this process continues by diffusion of the constituent elements and segregation of liquid of the melt to create second and third solidification reigns that culminate in a final region B as depicted in Figure 2.5. Due to this progressive solidification, the difference in diffusion rates between liquid and solid will eventually result in an inhomogeneous distribution of constituent elements within a single crystal. This then results in variations in the

concentration of the constituent elements that contributed to the construction of the solidified crystal [10].

Research on dendritic magnesium alloys AZ91D and AM60B containing aluminum and zinc revealed that their concentrations were low in the dendrite center and gradually increased toward the dendrite periphery [13]. The discovery was made by conducting SEM/EDS analysis on a number of 10 μm -apart spots on the tested specimen.

Optical microscopy can also demonstrate this nonhomogeneous micro-distribution. The alloy response to etching is extremely dependent on alloy content, and grain boundaries are not revealed due to the inhomogeneous micro distribution within the dendrite [10]. The direction of the chemical composition gradient within the dendrite determines whether the dendrite has a darkened center or darkened periphery when viewed metallographically. This metallographic appearance is referred to as "Coring" and can be eliminated by a homogenization thermal treatment that redistributes the constituent element and produces microstructure homogeneity [10].

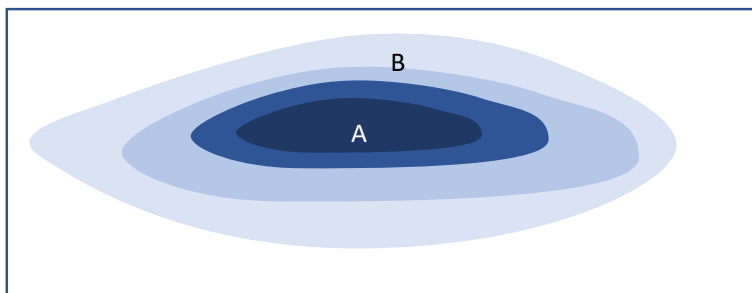


Figure 2-5: Coring in dendritic microstructure

2.3.2.1 Incipient Melting Point

Alloys Solidification is non equilibrium process. Thus, when the temperature of the molten substance falls below the liquidus temperature, solid particles develop in stages. Each newly developed solid particle's chemistry conforms to the solidus line of the alloy phase diagram as solidification continues. Because the solid's diffusivity is slower than its solidification rate, the solid's overall chemistry cannot reach equilibrium solidus. Consequently, a small quantity of liquid persists in the melt at the solidus temperature. At temperatures below the equilibrium solidus temperature, this liquid will begin to solidify, producing a eutectic product that is typically observed under high magnification. This lower temperature is known as the Incipient Melt Point (IMP) or nonequilibrium. Several methods exist for determining the IMP of an alloy, including the following [14]:

1. Heating the sample in isothermal furnace at certain temperature.
2. Maintaining the heating within specific time just to ensure sample achieved a uniform heat distribution.
3. Cooling the sample rapidly
4. Repeating the above steps with higher temperatures for different samples.
5. Performing metallography examination for the heated samples to identify the samples having indications of incipient melting (voids/eutectic phases).

The presence of small shrinkage porosities and the precipitation of fine eutectic phases within the microstructure of an alloy are metallographic indications of initiation of melting.

2.4 Homogenization Heat Treatment

Homogenization Heat Treatment is a common method for obtaining a uniform distribution of constituent elements and phases within the microstructure. As a consequence, homogenization heat treatment will improve the microstructure of dendrites through the following diffusion-related processes [14]:

1. Grain coarsening or recrystallization precipitation of supersaturated elements
2. Dissolution of unstable phases or precipitates
3. Coarsening/ spheroidization of stable intermetallic phases.

Due to the diffusion-dependent nature of homogenization heat treatment, its kinetics is determined by a number of variables, including temperature, diffusion distance, and diffusivity of the constituent elements. Prior to determining the temperature and duration of a heat treatment, the diffusion rate of the constituent elements and the condition of the treated microstructure must always be considered. Knowing the prior condition in this approximation is essential, as this microstructure condition will determine the final homogenized microstructure (concentration gradient and present phases) that will be attained based on the selected heat treatment parameters.

Mathematically determining the precise time and temperature required to develop a wholly homogeneous microstructure may be challenging [14]. This difficulty arises from the complexity of the alloys, which makes it difficult to determine the diffusivities of specific elements within a particular microstructure [14].

2.4.1 Homogenization Heat Treatment Parameters

To obtain an acceptable level of homogenization in an alloy with chemical composition inhomogeneity caused by dendritic formation, homogenization heat treatment can be applied. The implementation of the desirable homogenization heat treatment procedure will require the specification of certain parameters in order to achieve the intended treatment objective. First, the heating time, also known as the holding time, should be specified. In order to construct and estimate the homogenization time, a tracer diffusivity is introduced.

$$\frac{x^2}{D}$$

Where D is the diffusivity of the element and x is the diffusion distance (diffusion path). As mentioned previously, due to coring, the chemical composition of a single crystal at the center of a dendrite differs from that at the periphery of the dendrite. Consequently, x is regarded as the distance corresponding to half the distance between two dendrite arms. This distance can be readily measured and determined using metallographic techniques. Consequently, the second step is to determine the diffusivity D by:

$$D = D_0 \exp \left(\frac{-Q}{RT} \right) \quad (2.3)$$

Where,

D_0 : is the frequency factor in (cm²/s).

Q: is the activation energy in (KJ/mol).

T: is the absolute temperature in (K).

R: is the gas universal constant 8.31 (J/mol K)

Since the focus of this research is the corrosion behavior of Sellite-6, which is dependent on the role of chromium, the homogenization heat treatment process will consider the homogenization of chromium within the alloy microstructure. Thus, the first two variables of this equation can be derived from data tables and graphs pertaining to the diffusivity of chromium in cobalt.

The final phase in establishing the homogenization heat treatment procedure is to determine the optimal homogenization heat treatment temperature. In practice, commercial ferrous and non-ferrous alloys homogenize at temperatures 25 °C to 50 °C below their IMP in order to prevent local melting during the heat treatment [14]. Typical commercial homogenization heat treatment temperatures for cast materials range from 100 °C to 200 °C below the alloy's IMP [14].

Notably, if the alloy contains relatively large soluble atoms, the slow segregation (diffusion) of these atoms will be the rate-limiting step in the homogenization heat treatment procedure [14]. Refractory elements such as molybdenum and tungsten, for instance, have a slow diffusion rate in 316 stainless steel, necessitating a prolonged homogenization heat treatment time and a higher temperature. As shown in Figure 2.6, the solidus temperature of stainless steel 316 °C is 1393 °C, and its IMP temperature is typically 100 °C to 200 °C below the solidus temperature [14]. Taking the IMP of this alloy to be 1243 °C, it is annealed at 1177 °C with an x value of 100 °C to 200 m [25].

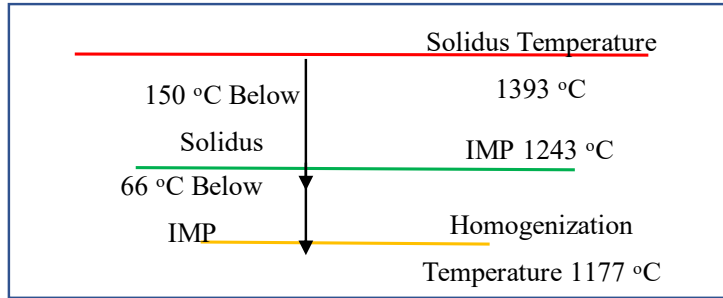


Figure 2-6: Stainless steel 316 homogenization heat treatment and IMP

2.5 Stellite-6 Alloy Homogenization heat treatment

In order to preserve their rigid microstructure, which is the source of their wear resistance, commercial Stellite alloys are typically not subjected to homogenization heat treatment during manufacturing. In other words, no literature references recommend a homogenization heat treatment temperature for these alloys. In this investigation, the required homogenization heat treatment temperature of Stellite-6 will be determined experimentally.

Once the Stellite-6 IMP and homogenization heat treatment time have been determined, a homogenization heat treatment temperature 20 °C to 50 °C below the IMP can be selected. By obtaining these parameters, a homogenization heat treatment procedure for the alloy under test can be established and implemented in order to attain the goal of this study.

CHAPTER 3

LITERATURE REVIEW

Researchers have studied the corrosion resistance of various Stellite alloys based on the method by which the Stellite layer is deposited on the substrate material (welding/casting process), the modification of certain parameters within a deposition method, and the modification of the chemical composition of the Stellite alloys. This section discusses the effect of varying depositing method in conjunction with varying clad alloy chemical composition and the impact of varying certain depositing method parameters on the corrosion performance of various clad overlay alloys.

3.1 Deposition Method/Chemical Composition Effect

Erosion-corrosion behavior was studied for Stellite-1, 6, 12, and 21 produced by the Hot Isostatic Pressing (HIP) Process and compared to the same alloys but welded with TIG [3]. The research was conducted in tap water and a 5% solution of nitric acid containing alumina particles. The metal loss of Stellite alloys produced by HIP was less than that of those produced by TIG, with the exception of Stellite-12, which has the same metal loss by both procedures. Metallography analysis revealed that all HIPed samples have more uniform carbide precipitation in terms of size and distribution than TIG welded samples. The HIPed microstructure consists of fine globular carbides that have been uniformly disrupted, resulting in a homogeneous microstructure. Stellite-1 had the highest erosion-corrosion resistance, followed by Stellite-12 and Stellite-6. As stated, this behavior was a result of the alloys' carbon, chromium, and tungsten content variations, which form the

carbides responsible for enhanced erosion-corrosion resistance. Due to the fact that the HIPing procedure creates a uniform microstructure, it provides alloys with superior erosion-corrosion resistance [3].

However, alumina particles were utilized in this study to accelerate metal removal from the protective coatings covering the surface of the tested alloys. This method may enable a precise interpretation of the erosion effect, but it may obscure a precise evaluation of the electrochemical behavior of the tested alloys resulting from their interaction with nitric acid.

Using the Potentiodynamic polarization method, Jianhua Yao [15] observed equivalent corrosion resistance and stable passivity in Stellite -22, Stellite-21, and Stellite-728 in 3.5% NaCl, 11.5% H₂SO₄, 1.2% HCl, 1% FeCl₃, and 1% CuCl₂ solutions at room temperature. As shown in Table 3.1, these three alloys have nearly identical chemical compositions, with the exception of Stellite-21, which contains 5.5% molybdenum compared to the other two alloys which contain about 11%. Stellite-22 and Stellite-728 are more susceptible to pitting corrosion due to the instability of the protective chromium oxide film (the presence of a hysteresis loop in the cyclic polarization curve), as disclosed by cyclic polarization analysis. In contrast, Stellite-21 demonstrated a capacity for rapid recovery and formation of its protective oxide film. The positive behavior of Stellite-21 is attributed to the small volume fraction of the chromium-rich carbide that precipitated. As depicted in Figure 3.1, SEM/EDS analysis of Stellite-21 revealed the presence of small areas of precipitate composed of chromium-rich carbide and molybdenum-rich intermetallic compounds. In contrast, the addition of molybdenum to the other two overlay alloys led to the formation of intermetallic carbides and molybdenum-rich intermetallic compounds in relatively

extensive areas. The reduction of this carbide volume fraction in Steillite-21 led to the homogeneity of the protective chromium oxide film, which was advantageous for the overlay alloy's rapid film formation.

Table 3-1: Stellite alloys-21, 22 and 728 overlay alloys chemical compositions [15]

Overlay Alloy	Element %								
	Cr	Mo	Ni	Fe	C	Si	Mn	Nb	Co
Stellite-21	27.0	5.50	2.53	0.85	0.25	1.49	0.46	-	61.92
Stellite-22	27.0	11.0	2.75	3.00	0.25	1.00	1.00	-	54
Stellite-728	24.0	11.8	3.80	1.00	0.35	0.45	0.52	2.07	56.01

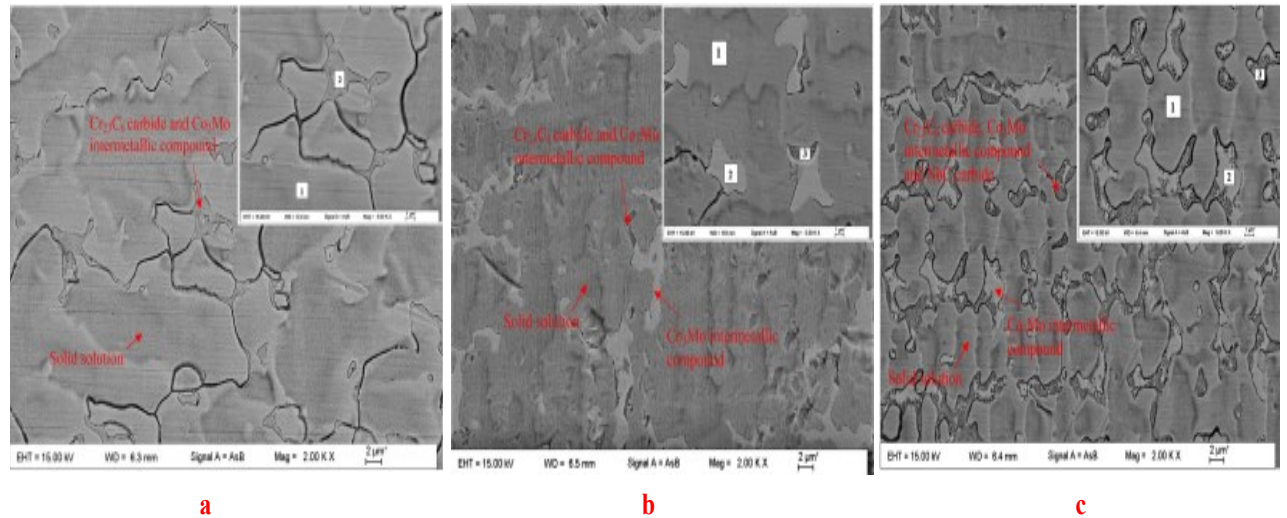


Figure 3-1: Microstructure of (a) Stellite-21, (b) Stellite-22 and (c) Stellite-728 [15]

Malayoglu and coworkers [5] discovered that the corrosion resistance in alkylne solution 3.5% NaCl at temperatures between 30 °C and 90 °C of Stellite-6 produced by HIPing is substantially higher than that of Stellite-6 produced by conventional casting, which is consistent with [3]. The enhanced corrosion resistance of HIPed Stellite-6 was attributed to the type, size, and shape of the carbides produced by the two distinct deposition

techniques. In their analysis, they found spheroidal carbides uniformly distributed along the entire microstructure generated by the HIPing process, whereas conventionally cast Steillite-6 produced coarse carbide islands occupying the dendritic grain boundaries. However, they had difficulty interpreting the type of carbides detected by XRD analysis conducted on both HIPed and conventionally cast Stellite-6 samples. The alleged difficulty resulted from the overlap of the intensities of various types of carbides at the same two angle on the XRD curve. The authors cited scholarly articles to support their claim that carbides precipitated by HIPing conform to chromium-rich carbides (M_7C_3 and $M_{23}C_6$) as opposed to refractory elements carbides (MC) precipitated by conventional Steillite-6 deposition. In conclusion, the high corrosion resistance of HIPed Steillite-6 was attributed to the presence of fine spheroidal chromium carbides, which contain a greater quantity of chromium and improve the stability of the passive alloy film.

Figure 3.2 demonstrates that the microstructure of Hot Wire TIG Stellite-6 overlay versus Lost Wax Cast (LWC) Stellite-6 on low alloy steel substrate consists primarily of primary cobalt-rich dendrite [16]. As shown in Figure 3.2(a), chromium-rich carbides precipitated in a fine morphology surrounding the primary cobalt-rich matrix in TIG-welded overlay Stellite-6. Figure 3.2 (b) shows that LWC produced larger chromium-rich carbide as well as larger tungsten-rich intermetallic phases. The overlay cladding alloys were then subjected to erosion-corrosion tests at 37 °C to 40 °C in a 3.5% NaCl solution containing spherical silica sand. The efficacy of the overlay alloys was then evaluated under three test conditions (static, liquid impingement, and solid-liquid impingement) as outlined in Table 3.2. In all test conditions, the results indicate that the erosion-corrosion resistance of LWC is superior to that of Steillite-6 TIG overlay. In static and liquid impingement conditions,

for instance, the erosion-corrosion rate of the welded overlay is greater than that of the cast one. The poor erosion-corrosion behavior of the TIG-welded overlay was attributed to the effect of dilution caused by the diffusion of chromium and nickel from the overlay layer into the substrate, which decreased the erosion-corrosion resistance of the overlay. The dilution was demonstrated by comparing the chemical composition of the Stellite overlay feed stock to the composition of the Stellite overlay after deposition, as shown in Table 3.3 [16]. Nevertheless, based on this analysis, the diffusion of iron from the overlay layer into the substrate alloys was found to be quite significant. Therefore, the dispersion effect on corrosion resistance can be viewed not only as the loss of corrosion-resistant elements, but also as the introduction of corrosive elements.

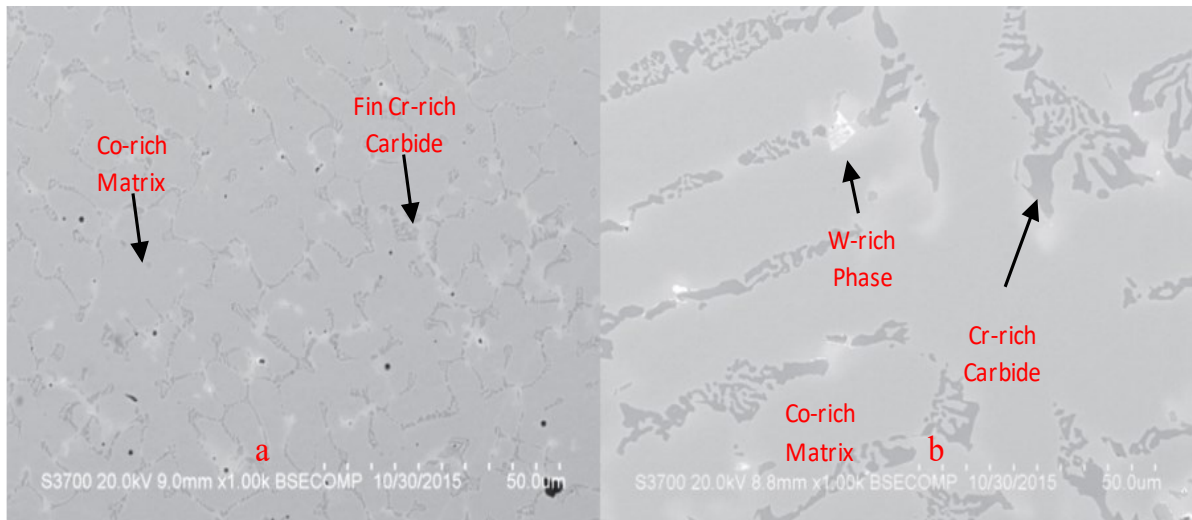


Figure 3-2: Stellite-6 microstructure (a) TIG welding and (b) LWC [16]

Table 3-2: Stellite -6 TIG welding and LWC alloys mass loss [16]

Material	Mass loss (mg/h) Static condition	Mass loss (mg/h) Liquid impingement condition	Mass loss (mg/h) Solid-liquid
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			impingement condition
Double Layer Stellite-6	0.15	0.089	0.35
Single Layer Stellite-6	0.15	0.059	0.18
Lost Wax Cast Stellite-6	0.0013	0.004	0.18

Table 3-3: Stellite -6 TIG welding and LWC overlay dilution measurements [16]

Overlay Alloy	Chemical Composition								
	Si %	Cr %	Mn %	Fe %	Ni %	Mo %	W %	C %	Co %
Feedstock	2.00	30.0	0.50	3.00	3.00	1.00	5.00	1.22	54.28
Single Layer Weld Overlay	0.99	23.2	0.92	20.07	0.04	0.02	3.89	0.89	49.98
Double Layer Weld Overlay	1.13	24.2	0.93	18.2	0.04	0.02	3.76	0.90	50.82
LWC	0.85	29.0	0.28	2.66	1.92	0.69	4.77	1.13	58.7

The corrosion and abrasion resistance of Steillite-6 was also investigated in 0.6 M NaCl naturally aerated solution at 25 °C [17]. Carbon steel substrate was coated with Steillite-6 alloys using High Velocity Oxygen Fuel sprinkling technologies (HVOF) and GTAW cladding overlay method. HVOF generated a laminar structure, whereas GTAW generated coarser dendrites microstructures with large concentrations of iron and Cr_7C_3 carbides. In addition, the overlay layer produced by HVOF had microscopic pores and interlamellar oxides, whereas the overlay layer produced by GTAW did not. Thus, the porosities and

interlaminar oxides in the HVOF veneer layer manifested as defects and discontinuities, reducing its corrosion resistance to the same level as the carbon steel substrate. In contrast, the GTAW overlay layer demonstrated adequate corrosion resistance.

Kim H.-J. and Y.J. Kim [18] studied the corrosion resistance in 3% NaCl at room temperature of Stellite-6 and Mecto-16C (Ni base) overlaid on a low carbon steel substrate by Plasma Transfer Arc welding (PTA) and compared it to the same alloys overlaid by Spry and Fused Open Arc (SFOA) welding process. In general, it has been observed that the corrosion resistance of Stellite-6 and Mecto-16C deposited via PTA is greater than that deposited via SFOA welding. In Metco-16C, the corrosion resistance of PTA is greater than that of SFOA, despite the fact that PTA welding resulted in greater dilution than SFOA welding. This is due to the formation of pores at the carbide-matrix interfaces caused by SFOA welding. In addition, the corrosion resistance of Stellite-6 produced by PTA was greater than that produced by SFOA due to the fact that PTA produced less dilution than the SFOA welding process.

In addition, Ugur Malayoglu and Anne Neville [3] examined the erosion-corrosion resistance of Stellite alloys-6 and 706 that were cast and HIP-coated. They examined the effect of tungsten and molybdenum as alloying elements in the investigated cladding alloys (Table 3.4). The HIPing process resulted in the formation of fine and uniformly distributed carbide in both Stellite cladding alloys as a consequence of the disparate methods by which they were deposited. However, due to the presence of molybdenum, Stellite-706 displayed both chromium-rich and molybdenum-rich carbides, whereas Stellite-6 displayed only chromium-rich carbides. In conclusion, the HIPed Stellite-6 and 706 performed better than their cast counterparts in the erosion-corrosion test, as indicated by less metal loss.

Comparing Steillite-6 and 706, the latter was found to possess the highest erosion-corrosion resistance of the two. This observation led to the conclusion that molybdenum has the most significant effect on enhancing the erosion-corrosion resistance of the overlay alloy in the type of carbide precipitate (molybdenum-rich carbide) it is precipitated from. In contrast, tungsten was found to have no effect on Steillite-6's erosion-corrosion resistance [19].

Nevertheless, according to [17], an increase in molybdenum above 5% can result in the formation of extensive areas of molybdenum-rich carbide in the overlay alloy's microstructure. This will increase the volume fraction of the chromium-rich carbide that results in an inhomogeneous protective oxide film and pitting corrosion.

Table 3-4: Stellite alloys-6 and 706 overlay alloys chemical compositions [3]

Overlay Alloy	Overlaying Method	Elements %						
		Co	Cr	W	C	Fe	Ni	Mo
Stellite 6	HIPed	60.9	29	4.4	1.1	1.8	2.5	0.3
	Cast	64.3	27.6	4.8	1.1	0.8	0.8	0.6
Stellite 706	HIPed	60.9	28.2	0.1	1.2	1.7	2.4	5.5
	Cast	60.8	28.6	0.1	1.3	1.5	1.6	6.1

In an effort to enhance the mechanical and corrosion properties of Stellite-6, powdered tungsten carbide (WC) was combined with it [20]. Then, this composite cladding was applied using laser cladding technology to low carbon steel. The quantity of WC utilized was 30% of the Stellite-6/WC mixture and was compared to a mixture created by combining 60% of the Stellite-6/WC mixture. In both types of mixtures, it was discovered that the amount of primary WC precipitated is inversely proportional to the laser beam power. Nevertheless, regardless of the laser beam intensity employed, a 60%WC mixture was observed to result in a greater number of primary tungsten carbides precipitating within

the cladding alloy microstructure, resulting in a clad layer with cracks and pores. Thus, it was deduced that the evolution of the deteriorated cladding was influenced by the increasing carbide content. In addition, the author established a correlation between the observed cracks and porosities and the difference in thermal expansion between the precipitated tungsten carbides and the cladding alloy matrix, which consists primarily of cobalt solid solution [20].

Comparing the corrosion behavior of conventional Stellite-6 in a 5% NaCl solution at 22 °C with the composite cladding Stellite-6 containing 60% WC, the corrosion resistance of conventional Stellite-6 was determined. Unexpectedly, it was discovered that the composite cladding material Stellite-6 with 60% WC has a reduced corrosion resistance. This behavior was attributed to the accumulation of tungsten carbide in the microstructure of the cladding alloy [20].

However, tungsten carbide precipitation in large quantities may be viewed as an advantage for corrosion resistance because its precipitate can prevent the formation of chromium carbide, which negatively affects corrosion resistance.

3.2 Effect of Deposition Parameters

Chandran, S., and colleagues [4] investigated the impact of expanding the overlay thickness on dilution and corrosion behavior. The corrosion behavior of Colmonoy-6 (73.5% Ni, 13.56% Cr, 4.75% Fe, and 4.23% Si) overlaid on 316LN stainless steel substrate in 0.004% nitric acid at 65 °C was investigated. In their study, they evaluated the corrosion resistance of Colmonoy-6 overlays deposited in one, two, three, four, and five layers using the GTAW welding process. They concluded that the effect of dilution on corrosion resistance was almost negligible for overlays with more than two layers, while single- and double-layer

overlays exhibited poor corrosion resistance due to the dilution effect. However, and as they stated, cladding by weld overlay is typically limited to a maximum thickness of 2 to 3 millimeters, as a consequence of the high hardness and brittleness of the overlay [4].

In addition, various heat treatment processes, such as Post Weld Heat Treatment (PWHT) and pre-heating, were observed to have no adverse influence on the corrosion resistance of Stellite-21 welded with GTAW [9]. It was observed that pre-heating at temperatures of 500 °C and 400 °C and PWHT at temperatures of 500 °C and 600 °C were unable to eliminate or reduce the effect of dilution, thereby failing to enhance the corrosion resistance of the investigated overlay alloy [21].

3.3 Literature Review Outcomes

From the preceding discussion, it is clear that corrosion resistance studies of overlay cladding alloys focused on the effect of dilution and the overlay microstructural characteristics associated with its deposition. Dilution was observed to cause chemical composition variation within the matrix of overlying alloys, thereby decreasing their corrosion resistance. The effect of dilution was evaluated primarily on the outer surface of the final layer of the clad overlay. In terms of corrosion risk, the interface zone between the substrate and the first clad layer is the most vulnerable area. Since it involves the heat affected zones of the overlay clad and the substrate alloys, the corrosion resistance of the interface zone can deteriorate significantly. This deterioration occurs because this zone will exhibit the highest levels of dilution or microstructural alterations in general. As described in section 2, the interface region of the studied system encountered the most severe corrosion attack. As a result, this work intended to concentrate on this topic in particular.

In addition, the majority of the corrosion studies summarized above evaluated corrosion using alkyl solutions or acids with relatively low concentration. These environments may not be representative of the corrosion performance of the material because they are not as aggressive as those used to evaluate the corrosion resistance of alloys. Conducting corrosion experiments in concentrated acids may induce the ultimate corrosion behavior of the tested alloy and provide a clear indication of its resistance.

The reviewed studies highlighted the impact of deposition method and parameters on the microstructure of the clad overlay. When chromium carbides precipitate in fine morphology, the overlying alloy demonstrates relatively high corrosion resistance in test environments. This enhancement in corrosion resistance is attributable to the homogeneity of the chemical composition of the overlay alloys, which is associated with the formation of fine chromium carbide. Thus, one can conclude that heat treatment can be used to alter the carbide morphology and enhance the corrosion resistance of overlay clad alloys. In addition, heat treatment can play an important role in regulating and minimizing the clad overlay dilution, as described in section earlier.

It was discovered that increasing the thickness of the clad overlay layers was an effective method for minimizing the extent of dilution. This is because increasing the thickness provides a longer path for diffusion, as described in Section 2.3.1.3 (Equation 2.2), and consequently the elemental concentration gradient is reduced, resulting in a decrease in dilution amplitude. However, increasing clad overlay thickness beyond a certain limit is impractical because, as clad overlay thickness increases, so does hardness, rendering the overlay layer more brittle and less cohesive.

CHAPTER 4

OBJECTIVE

The technology of Stellite provided vast advantages, and therefore, its uses have extended tremendously. Today, components coated with Stellite alloys can be found in a variety of industries, such as tool manufacturing, automotive, oil, petrochemical, and even aerospace. Degradation of the coating causes, as a result, undesired safety or financial consequences. Researchers focused their studies on the corrosion resistance of the surface of the Stellite coating without addressing how the interface between the coating and the substrate will act in corrosive environments.

The objective of this study is to investigate the corrosion behavior of the interface zone of the welded Stellite-6 overlay onto a 304L stainless steel substrate in 40% concentration of nitric acid at 25 °C.:

1. Measure the corrosion rate of the of the overlay, substrate, and interface zone of the Stellite-6 overlay/304L stainless steel substrate system.
2. Studying the galvanic corrosion possibility between the interface zone, Stellite-6 overlay, and 304L stainless steel.
3. Studying the effect of heat treatment on corrosion resistance of the interface zone.

CHAPTER 5

EXPERIMENTAL METHODOLOGY

5.1 Material

In this study, investigated specimens will be prepared from a valves taken from HNO₃ production plant. These valves were exposed to an environment containing HNO₃ and having a varying concentration that reaches 40% and temperature not exceeding 40 °C. Among the valves' internal parts, the gate of the valves then was split into number of specimens. The gate is made from 304L stainless steel and overlaid by one layer, 2 mm thick, of Stellite-6 alloy using the Gas Tungsten Arc Welding (GTAW) technique. [Tables 5.1](#) and 2 show the typical chemical composition of the 304L stainless steel and Stellite-6 alloys.

Table 5-1: Chemical composition (wt.%) of 304L Stainless Steel

Element	Fe	Cr	Ni	Mn	Si	C	P	S
Wt.%	Bal.	18-20	8-13	2 max.	1 max.	0.03 max.	0.05 max.	0.03 max.

Table 5-2: Chemical Composition of Stellite-6 Overlay Alloy

Element	Co	Cr	W	C	Fe	Ni	Mo	Si	Mn
Wt.%	Bal.	27-31	3.5-5.5	0.9-1.4	3 max.	3 max.	1.5 max.	1.5 max.	1 max.

5.2 Characterization

5.2.1 Before Heat Treatment

SEM elemental liner scan and mapping analysis will be performed for specimen on the surface that include the interface zones to study the liner elemental variation of chromium. By this analysis, the concentration gradient of the diffused elements can be detected. Additionally, SEM area mapping and EDS analysis will be used to give an idea about the composition of the carbide and the precipitated phases within the microstructure.

5.2.2 After Heat Treatment

The above SEM analysis will be repeated for specimens that are subjected to heat treatment. In this examination, changes in the morphology, amount and size of the carbides and precipitated phases will highlighted and correlated to the corrosion behavior of the interface zone. Also, SEM mapping at this stage, will show the constituent elements redistribution and measure the concentration gradient change of these element.

The interface zone of corroded sample will be examined by optical microscopy to study the type and severity of the corrosion after exposing the examined specimens to the corrosive environment. The optical microscopy will focus to determine if the corrosion attack is uniform or localized (intergranular-transgranular) among the two alloys interface zone.

5.3 Hardness Measurements

Specimens mounting, surface preparation and hardness measurements were performed according to ASTM E384-11 (Standard Test Method for Knoop and Vickers Hardness of Materials). Hardness testing in this study will be performed in two stages. First, for the as

procured specimen and second for specimen subjected to heat treatment. A comparison of the revealed hardness values then will be considered to explain the heat treatment effect on Steillite-6 alloy hardness. Using Vicker-10 scale, the measurements were performed for each specimen considering 5 readings. The average of these 5 readings and the standard deviation (STD) vales were calculated to represent the hardness of the examined specimens.

5.4 Corrosion Tests

5.4.1 Solution Preparation

A solution consists of nitric acid having 40% concentration is selected to study the corrosion behavior of the tested material in this work. Nitric acid is available commercially with a concentration of 69%. Therefore, the required concentration for this examination will be prepared by mixing that commercial nitric acid with distilled water to reach the required 40% concentration according to:

$$C_1 V_1 = C_2 V_2 \quad (5.1)$$

Where:

C_1 : Acid concentration (69%)

V_1 : Volume of nitric acid having (69%) concentration

C_2 : Required acid concentration (40%)

V_2 : Volume of required nitric acid (1 L)

Solving for V_1

$$V_1 = \frac{C_2 V_2}{C_1} = \frac{(0.40)(1)}{(0.69)} = 0.580 \text{ L}$$

Finally, potable water having a volume of $1 - 0.580 = 0.42 \text{ L}$ will be mixed with V_1 to obtain the required nitric acid concentration.

This concentration is selected because it was shown in the preliminary examination of this work that both tested materials (stainless steel 304 L and Stellite-6) did not exhibit a passive behavior during the Potentiodynamic Polarization testing. Rather they showed an active behavior curve. Due to this behavior, linear Polarization resistance (LPR) methodology will represent a reliable means of calculating the corrosion rate in mm/year [22].

5.4.2 Corrosion Rates Measurements

Working electrodes that represent the stainless steel 304L, Stellite-6 alloys, and interface zone will be prepared according to ASTM G-01 considering the surface polishing addressed by this methodology by which silicon carbide polishing papers having a grit size of 240 to 600 in sequence will be used followed by specimen water washing and drying. Then LPR analysis of these surfaces will be performed according to ASTM G-59 to calculate the corrosion rates of each working electrode in the selected corrosive environment. This means that three specimens will be examined and the corrosion rate of these specimens will be calculated individually. In this study, *Corrtest* CS 350 will be utilized for the interned corrosion analysis.

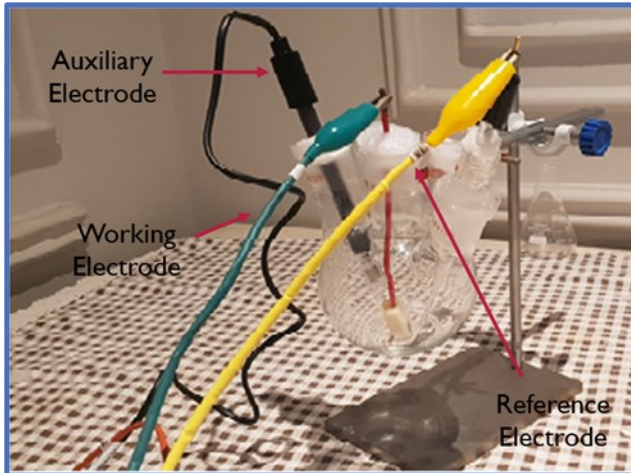


Figure 5-1: Corrosion testing cell

In the LPR test, three-electrode procedure consisting of:

1. Working electrode (test specimen).
2. Reference electrode of type Saturate Calomel Electrode.
3. Platinum counter (Axillary) electrode.

The three-electrode experiment assembly is shown in [Figure 5.1](#). The Open Circuit Potential (OCP) of the system will be monitored for a period of 1 hour to ensure the stability of the monitored OCP. Then, the system will be polarized in Potenteodynamic Polarization (PDP) mode to a voltage rage of -0.25 V below OCP and +0.25 V above OCP and maintaining the increase in voltage (voltage frequency) to be limited to 0.166 mV per second . As a result, the polarization resistance R_p will be obtained by taking the slope of the LPR curve in a narrower voltage range such as -0.01 V below OCP and +0.01 V above OCP. Finally, the polarization resistance is converted mathematically to corrosion rate in mm/year according to :

$$\begin{aligned}
R_p &= \left[\frac{d\varepsilon}{di_{app}} \right]_{\varepsilon \rightarrow 0} = \left[\frac{\Delta\varepsilon}{\Delta i_{app}} \right]_{\varepsilon \rightarrow 0} \\
&= \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)} = \frac{B}{i_{corr}}
\end{aligned} \tag{5.2}$$

$$B = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \tag{5.3}$$

$$CR \left(\frac{mm}{year} \right) = I_{corr} \left(\frac{A}{cm^2} \right) \times \text{Wiegth Equivelenat/density} \times 365 \times 24 \times 3600 \tag{5.4}$$

5.4.3 Galvanic Corrosion Assessment

Galvanic corrosion between HAZ-1 and the -6 bulk alloy will be studied by the Zero Resistance Ammeter (ZRA) method. As part of the experimental set-up, two working electrodes will be prepared and mounted in the corrosion cell as shown in [Figure 5.2](#). The first working electrode W_1 will be selected to represent HAZ-1 and the second working electrode W_2 will represent the Stellite-6 bulk alloy. The reference electrode in this setup will be mounted in the salt bridge and its Luggin Capillary will be facing W_1 . The noise current and noise potential will be monitored (zero ammeter) as function of time. If the system display a positive current, then HAZ-1 is an anode and the current is following from it to W_2 .

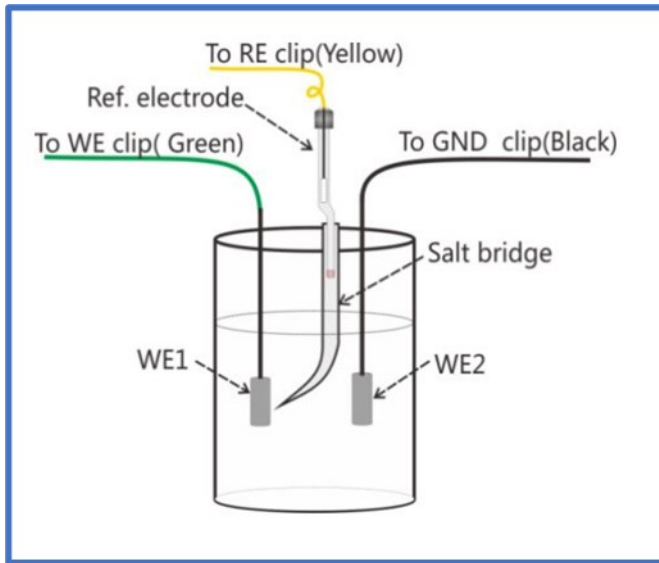


Figure 5-2: Galvanic corrosion test cell

5.5 Heat Treatment

In this part of the study, the effect of different heat treatment regimes (soaking temperature and time) on the Stellite-6's corrosion resistance will be investigated. Stellite-6 as can be seen in **Error! Reference source not found.**, is a cobalt chromium alloy. The phase diagram of cobalt chromium alloy is presents in Figure 5.3 which show at 30% chromium, a solidus temperature of 1425 °C this alloy. Considering the IMP temperature of this alloy will lie in a temperature range of 100 to 200 °C below the solidus temperature, 150 °C below the alloy solidus temperature can be selected. Thus, the heat treatment investigation can start with 1200 °C. then to examine the effect of different heat treatment regimes, different specimens will be subjected to a different heat treatment temperature under constant soaking time. The specimens were heated at a rate of 350 °C /h to the desired heat treatment temperature. Then, heating was held for 2 hours as soaking duration followed by water quenching to ambient temperature. In this experiment, Furnace NaberTherm was used.

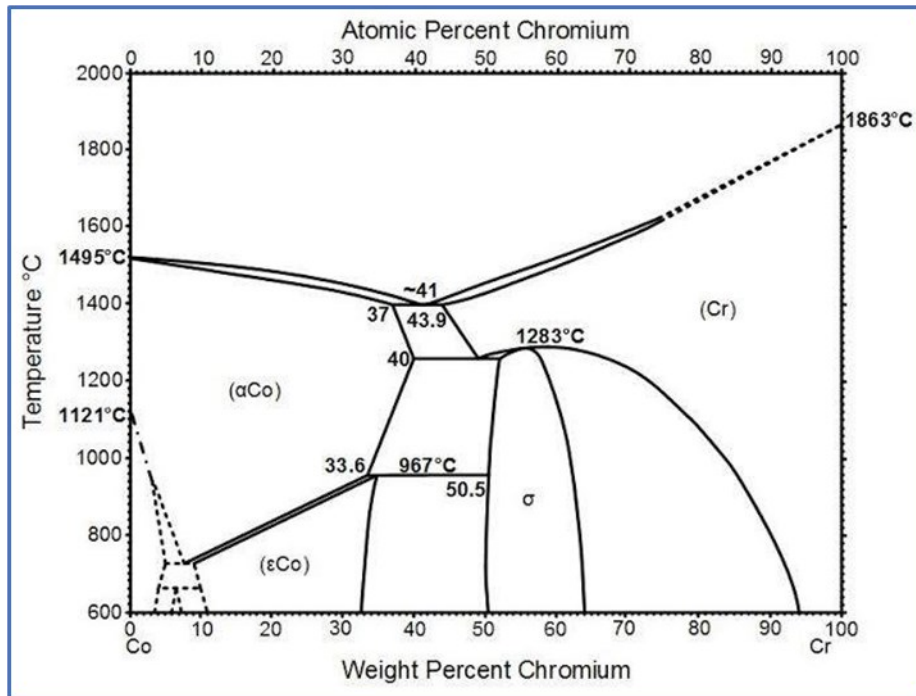


Figure 5-3: Cobalt-Chromium phase diagram

CHAPTER 6

CORROSION OF STELLITE-6 OVERLAY CLADDING

ON 304L STAINLESS STEEL IN NITRIC ACID

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6.1 Introduction

In the industries that produce nitric acid (HNO_3), austenitic stainless steels are employed in a range of parts, such as pressure vessels, pipes, and valves. Specific stainless steel grades, such as 304 and 304L, perform admirably over a broad temperature and HNO_3 concentration range. Their corrosion rates at low temperatures do not exceed 0.13 mm/y at HNO_3 concentrations ranging from 0 to 90% [1]. Furthermore, their corrosion rates remain moderate even when the temperature above the boiling point of HNO_3 when HNO_3 concentrations are kept below 50% [1]. These materials can be utilized to manage and store HNO_3 at various temperatures and concentrations due to how they respond in corrosion conditions [1].

Production facilities for HNO_3 contain many valves in various sizes. One of the common valve types utilized in these facilities is the gate valve. Typically, these valves are used to stop, control, and/or throttle the flow of process fluids. To minimize wear during use,

Stellite-type overlay alloys should ideally be applied to the interior valve components (gates, disks, guides, and seats), as shown in Fig. 6.1. The most popular metal alloy in these applications is thought to be Stellite-6, a cobalt-chromium-based alloy with excellent wear and corrosion resistance [2].

When internal valve components malfunction due to corrosion, there are considerable monetary losses, production losses, and expensive maintenance and replacement costs. When the concentration of HNO_3 is not greater than 40%, there have been numerous incidents of severe corrosion attacks on the internal components of 304L stainless steel valves covered in Stellite-6 alloy in HNO_3 manufacturing plants. It is interesting that the interface zone between the overlay and the substrate alloy was particularly vulnerable to corrosion attack in the observed failures, as shown in Fig.6.1a.

The dilution effect and chemical composition inhomogeneities that are present in the microstructure of Stellite alloys have a substantial impact on their corrosion resistance [3–9]. Researchers examined the impact of dilution on the corrosion resistance of Stellite alloys by concentrating on the factors that induce dilution, such as changing welding technique and parameters or the overlay thickness. As the dendrites grow in the interface zone, while the alloy is solidifying, welding, or casting, the overlay alloy may cause the chemical composition to be different in different places [10].

It was discovered that the corrosion resistance of the Stellite alloys is greatly impacted by an increase in dilution. The corrosion resistance of Stellite-6 in 3% NaCl overlaid on low carbon steel by plasma transfer arc welding (PTA) was investigated by Kim H.-J. et al. [18], who also compared it to the same alloy overlaid by spray and fused open arc (SFOA)

welding. Because the dilution associated with PTA is lower than that found in the SFOA welding process, the corrosion resistance of Stellite-6 manufactured by PTA was higher than that manufactured by SFOA. Additionally, in 0.001% HNO_3 , the impact of increasing the overlay thickness on the corrosion resistance of Colmonoy-6 overlay alloy was researched [4]. It was discovered that the overlay with more than two layers significantly improved corrosion resistance. Contrarily, because of dilution in the thin overlay, the overlay with single and double layers had poor corrosion resistance. However, due to its high hardness and embrittlement, weld overlaying is typically kept to a maximum thickness of 2–3 mm [4]. This is because a larger thickness might lead to cracking and spalling of the overlay.

The characteristics of the alloy microstructure created by a different way of overlaying were explored in relation to the impact of the chemical composition inhomogeneity of Stellite alloys on the corrosion resistance. When compared to the same Stellite alloys deposited by TIG welding, Wong-Kian et al. [3] found that the hot isostatically pressed (HIP) casting technique generates a homogenous microstructure that is reflected in strong erosion–corrosion resistance in a solution containing 5% HNO_3 . This result is consistent with the findings of the Malayoglu et al. study [5], which found that corrosion resistance in Stellite-6 with a 3.5% NaCl content generated using the HIPing method was much higher than that produced by conventional casting. According to their investigation, the HIPing technique created spheroidal, uniformly dispersed chromium carbides over the entire microstructure. In other words, the HIPing process made the microstructure more uniform, which made the material more resistant to corrosion [3, 6].

Studies of the interface zone between the Stellite overlay and the substrate alloys (stainless steel 304L) are scarce, even though corrosion resistance of the Stellite overlay's outer surfaces has received considerable attention. This investigation was conducted in order to determine what caused the internal parts (valve gate) of a gate-type valve manufactured of 304L stainless steel and overlaid by Stellite-6 to corrode. The investigation will concentrate on evaluating the corrosion rates, researching the mechanisms of corrosion in the interface zones, and contrasting them with those of 304L stainless steel that has not been overlaid with Stellite-6.

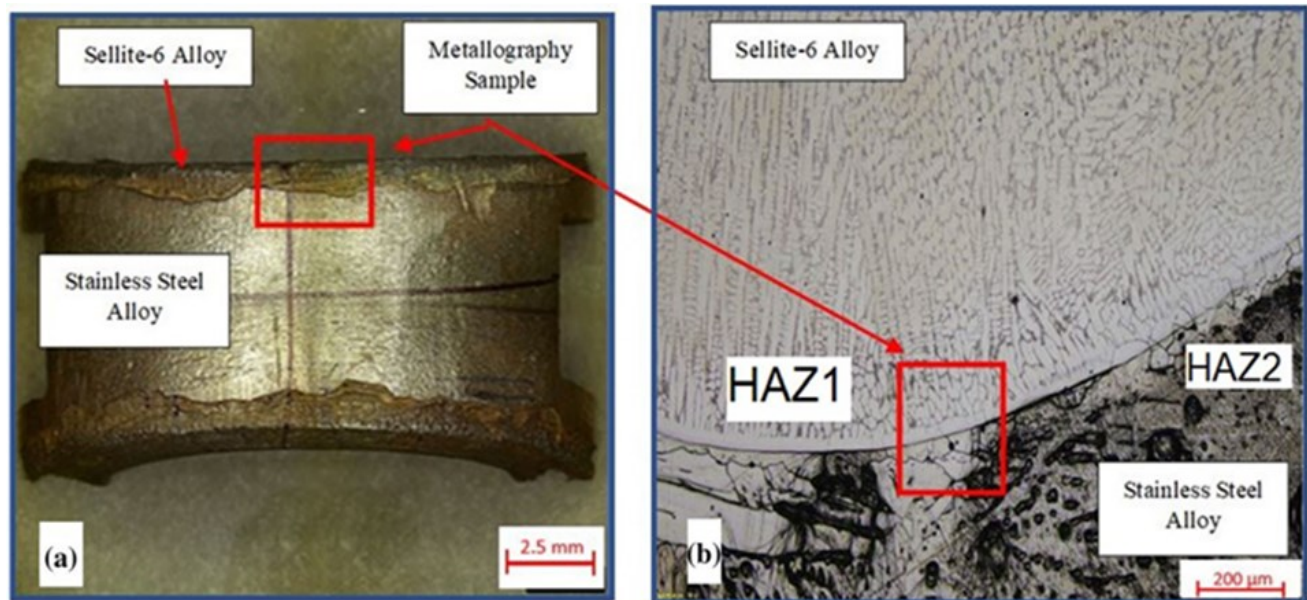


Figure 6-1: (a) Photograph image of the valve gate showing Stellite6 overlay cladding on 304L stainless steel, (b) optical micrograph of the welding interface showing HAZ1 and HAZ2

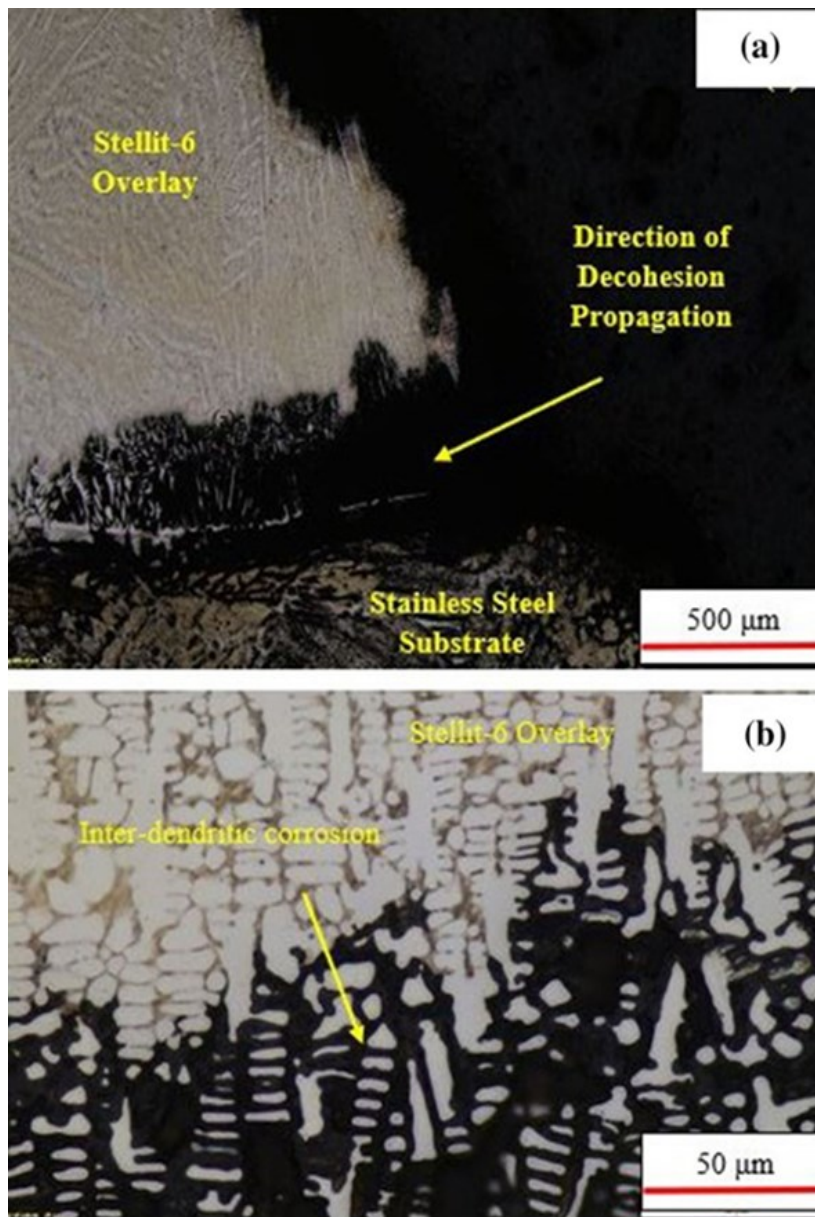


Figure 6-2: Optical micrograph of the corroded sample showing decohesion between the stainless steel and Stellite-6 overlay propagation initiation site

6.2 Results and Discussion

The optical micrograph for the failing area inside the examined valve gate is shown in Fig. 6.2. There is a visible corrosion attack in the area where the Stellite-6 overlay meets the stainless steel substrate. A separation (decohesion) of the overlay layer from the substrate is brought on by corrosion of HAZ-1 (on the Stellite-6 alloy region) in the interface zone, which is made up of two heat-affected zones, HAZ-1 and HAZ-2 (Fig. 6.1b). According to Fig. 6.2a, this decohesion appears to split the two connected alloys over their fusion line. Additionally, it is evident that HAZ1 corrosion started at the valve gate's exterior surface and spread laterally. While the stainless steel mating surface (HAZ-2) showed little to no metal loss, HAZ-1 underwent extensive corrosion. Figure 6.2 depicts inter-dendritic corrosion manifested by HAZ-1 under high magnification optical examination. Stellite-6 dendrites are separated from the main alloy's matrix. These findings imply that HAZ-1 experiences two different forms of corrosion: uniform corrosion, which results in substrate-overlay decohesion; and localized (inter-dendritic) corrosion, which is brought on by a full dendrite disengagement from the overlay alloy matrix.

6.2.1 Uniform Corrosion

Table 6-1, displays the outcomes of the LPR analysis performed on 304L stainless steel, Stellite-6, and HAZ-1 in 40% HNO_3 at 25 C. In comparison with the Stellite-6 (0.066 mm/y) and 304L stainless steel (0.0034 mm/y), the HAZ-1 showed the highest rate of corrosion (0.211 mm/y). Due to the difference in chemical composition, the corrosion rate of HAZ-1 would be significantly higher than that of 304L and Stellite-6. Chromium is the predominant element in chromium-containing alloys like stainless steel, providing the desired corrosion resistance in oxidizing conditions like HNO_3 [9]. The corrosion

resistance in concentrated HNO_3 acid also depends on the chromium content, which is true for Stellite alloys in diluted HNO_3 acid unless the alloy microstructure is sensitized due to the formation of the sigma phase or chromium carbide when the alloy contains a significant amount of carbon [6]. About 30% of Stellite-6 is made of chromium (Table 5-2), which contributes to the material's relatively high corrosion resistance as determined by the LPR (Table 6.3) and documented in the literature [9].

The EDS analysis (Figure 6-3) reveals that HAZ-1 has less chromium than the Stellite-6 bulk alloy. Because chromium is so important to corrosion resistance in oxidizing environments, the HAZ-1 would have less corrosion resistance because it has less chromium [9] [6].

Table 6-1: Outcomes of the LPR analysis

Specimen	$R_p \Omega/\text{cm}^2$	Corrosion Rate mm/y
304L stainless steel	78,395	0.0034
Stellite-6	2311	0.066
HAZ-1	995.11	0.211

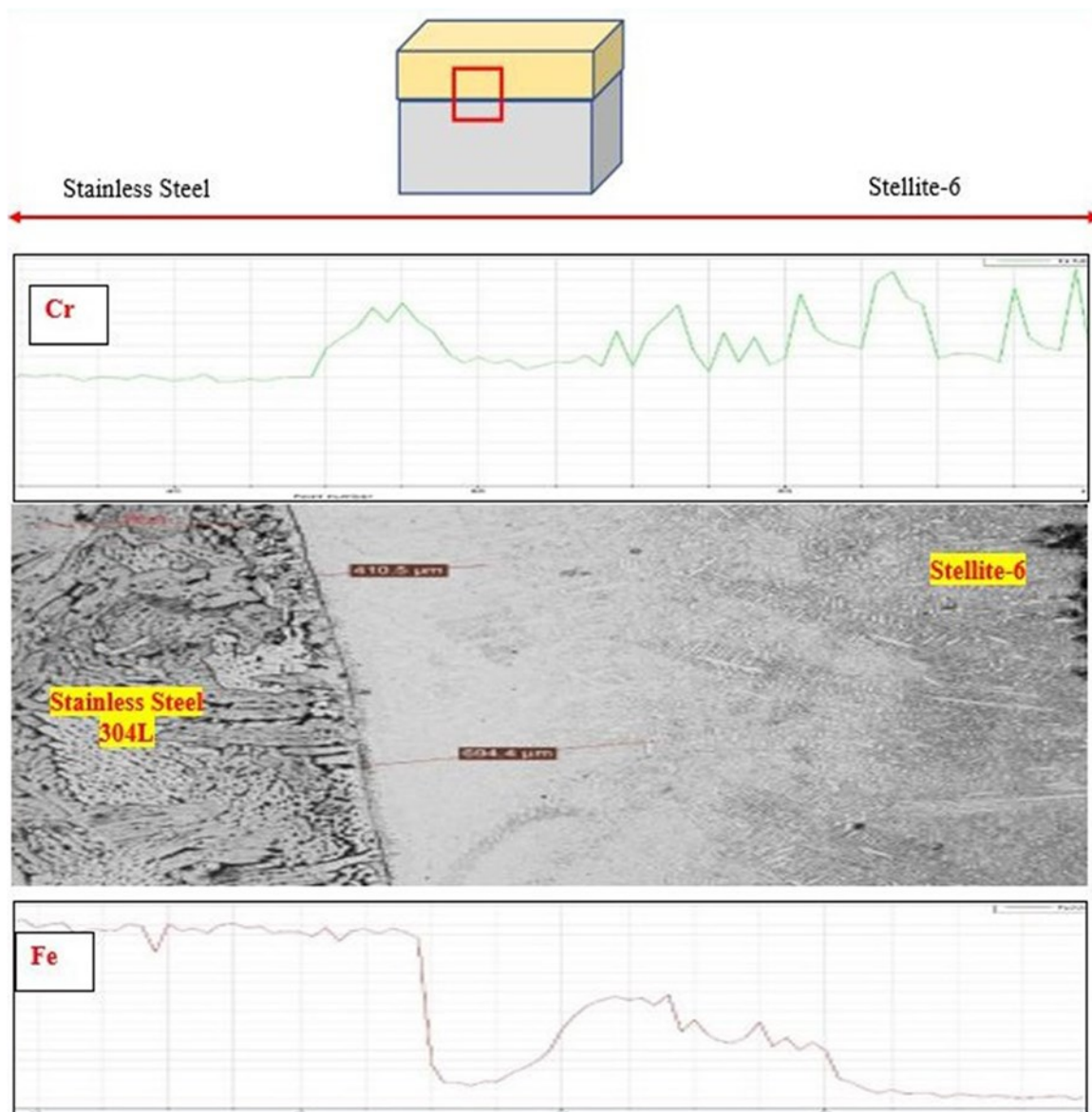


Figure 6-3: EDS analysis across the welding interface

6.2.2 Galvanic Corrosion

The need to investigate the potential of galvanic corrosion is raised since it appears that the corrosion is being caused by the differential in chromium content between HAZ-1 and its surrounding zones. ZRA analysis proved that galvanic cells were made between the HAZ-1 and the Stellite6 bulk alloy and between the HAZ-1 and the 304L stainless steel.

The ZRA study for the HAZ-1/Stellite-6 connection is shown in Fig. 6.4 The corrosion current travels from the HAZ-1 zone to the Stellite-6 zone, and its approximate value of 0.0276 A/cm^2 shows that the HAZ-1 behaved anodically with respect to the Stellite-6. As a result, HAZ-1 experiences galvanic corrosion. However, the investigation revealed a negative current of 0.0034 A/cm^2 in the HAZ-1/ 304L stainless steel connection (Figure 6-5). Therefore, there can be no development of galvanic corrosion cells between these two zones. In the end, in a galvanic corrosion mode, HAZ-1 broke down in relation to Stellite-6 rather than the substrate.

The decreased chromium content of HAZ-1 causes the galvanic corrosion cell to form between the HAZ-1/Stellite-6 zones, as demonstrated by the EDS study (Fig. 6.3). The diluting effect is mostly responsible for variations in chromium content [4]. The substrate, which has a lower chromium content than the overlay, is welded to it. As a result, atoms disperse from concentrated places to less concentrated ones [4]. Also, in this galvanic connection, HAZ-1 has a smaller surface area than the Stellite-6 overlay, which makes it corrode faster than the stainless steel substrate alloy.

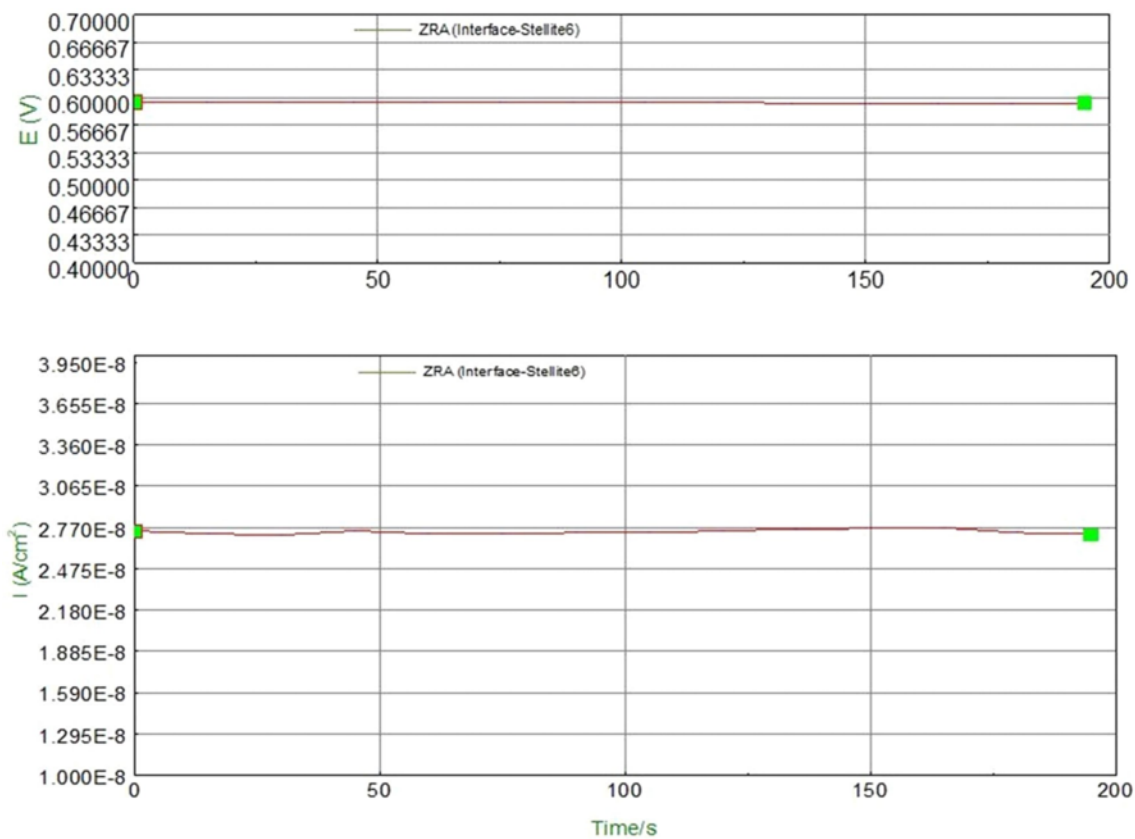


Figure 6-4: ZRA analysis for Stellite-6 and HAZ-1 coupling

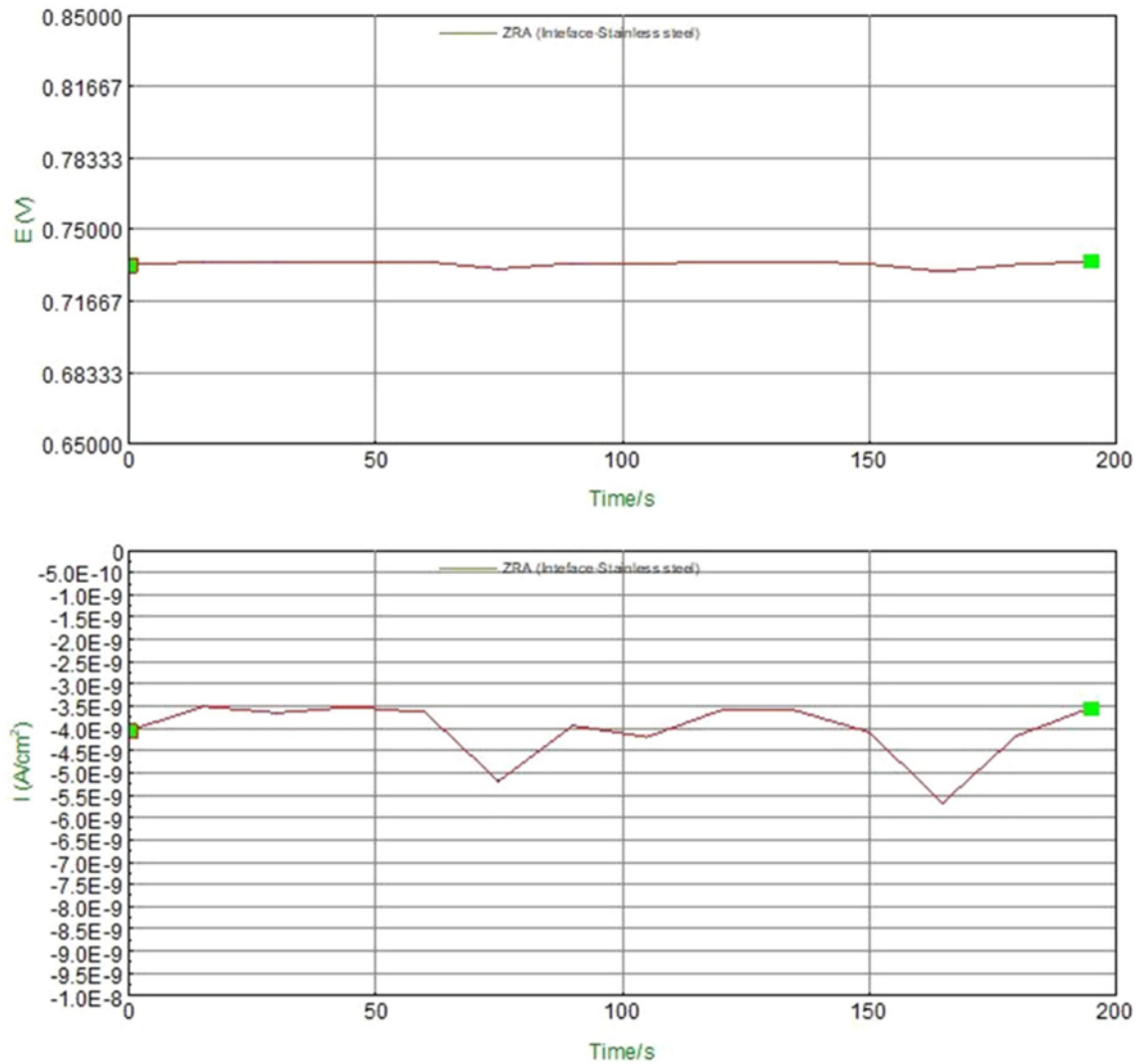


Figure 6-5: ZRA analysis for stainless steel and HAZ-1 coupling

6.2.3 Inter-dendritic Corrosion

A typical dendritic microstructure, consisting of a dendrite crystal surrounded by its borders, can be seen in the optical micrograph of the HAZ-1 (Figure 6-2). Eutectic phases are seen at the dendrites' peripheries (boundaries). As previously mentioned, HAZ-1 displayed an inter-dendritic corrosion type (Fig. 6.2), in which corrosion attacks dendrite peripheries more quickly than dendrite crystals. Therefore, it can be concluded that in the

examined environment, dendritic crystal exhibits higher corrosion resistance than dendrite peripheries. To study how the Stellite-6 alloy acts, it is important to know how the elements that make up the alloy are distributed inside the dendritic microstructure.

During the solidification, specific locations within the melt experience temperature declines below the liquidus temperature before the melt. At these locations, a solid particle forms as the nucleus of a newly crystallizing phase. The growth of the crystal phase nucleus will then be governed by the gradients in alloy concentration and temperature surrounding the nucleus [10]. When a crystal's nucleus is created, liquid from nearby regions will deposit on it and solidify to create the crystal's center, which is denoted by area A in Figure 6-6, until the ultimate crystal size is determined, this process proceeds via diffusion of the constituent elements and segregation of liquid from the melt to generate second and third solidification areas that lead to a final region B (Fig. 6.6). The differential in the diffusion speeds in liquid versus solid will eventually result in inhomogeneity in the distribution of the constituent elements within a certain dendritic matrix because of that gradual solidification. The concentration of the constituent elements involved in the creation of the solidified crystal varies because of this occurrence [10]. From this point of view, the chemical make-up of the dendrite boundary will be different from that of the dendritic crystal.

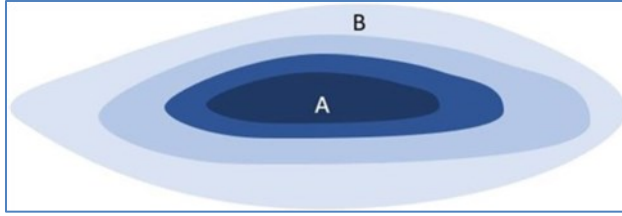


Figure 6-6: Inhomogeneity in dendritic microstructure

Mirshekari et al. [5] investigated the dendritic microstructure of Stellite-6 deposited by GTAW. According to XRD analysis, the alloy's primary phases are considerable amounts of carbides as well as solid solutions of γ -Co and ϵ -Co. This outcome is consistent with the analysis by Gholipour et al. [24]. The earlier work came to the qualitative conclusion that the primary hypoeutectic Co-rich phase dominates the dendrite crystal of Stellite-6, and the eutectic phases found in the inter-dendritic regions include chromium-rich carbides like M_7C_3 and $M_{23}C_6$. This finding was based on the chemical make-up of these two separate regions, which was determined by the EDS analysis, where it was discovered that the dendritic crystal conformed to fewer of the strong carbide formers like molybdenum and chromium. In other words, the formation and precipitation of the carbides are caused by the presence of carbide formers in the dendritic peripheries. The phase found in the inter-dendritic zone was further confirmed to be chromium carbide by EDS mapping, which also showed a higher density of chromium and carbon and a lower density of cobalt and iron [25].

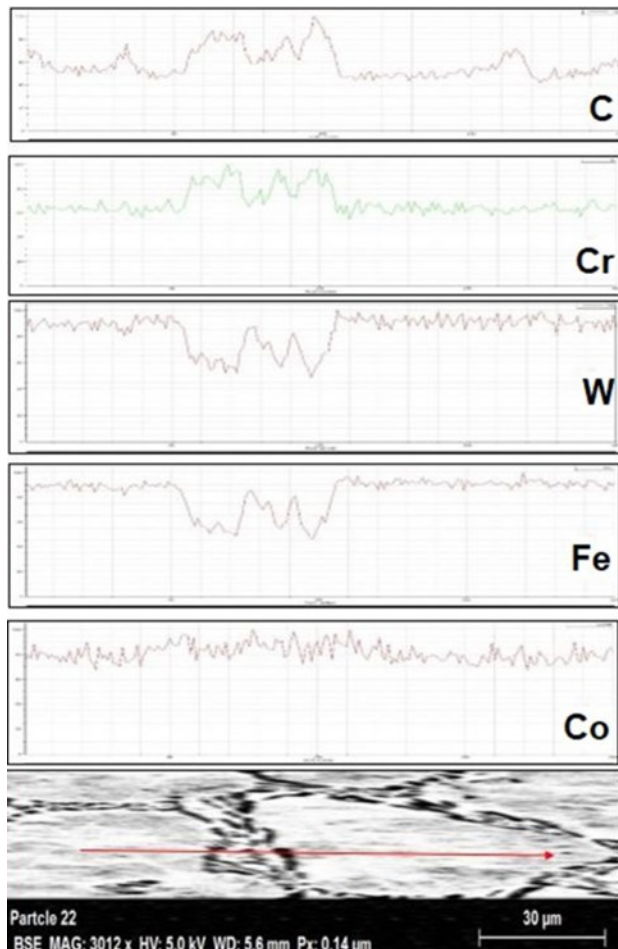


Figure 6-07: EDS Line scan across dendrite boundary

Additionally, linear elemental scanning across the dendrites of the specimen (Fig. 6.7) reveals a significant concentration of chromium and carbon there compared to the dendrite crystal. On the other hand, iron and cobalt are deficient in the inter-dendritic zones. Also, elemental mapping (Fig. 6.8) showed that there was carbon and chromium in the spaces between the dendrites. This shows that the eutectic phase in those spaces is mostly made of chromium carbide, which is in line with studies [25].

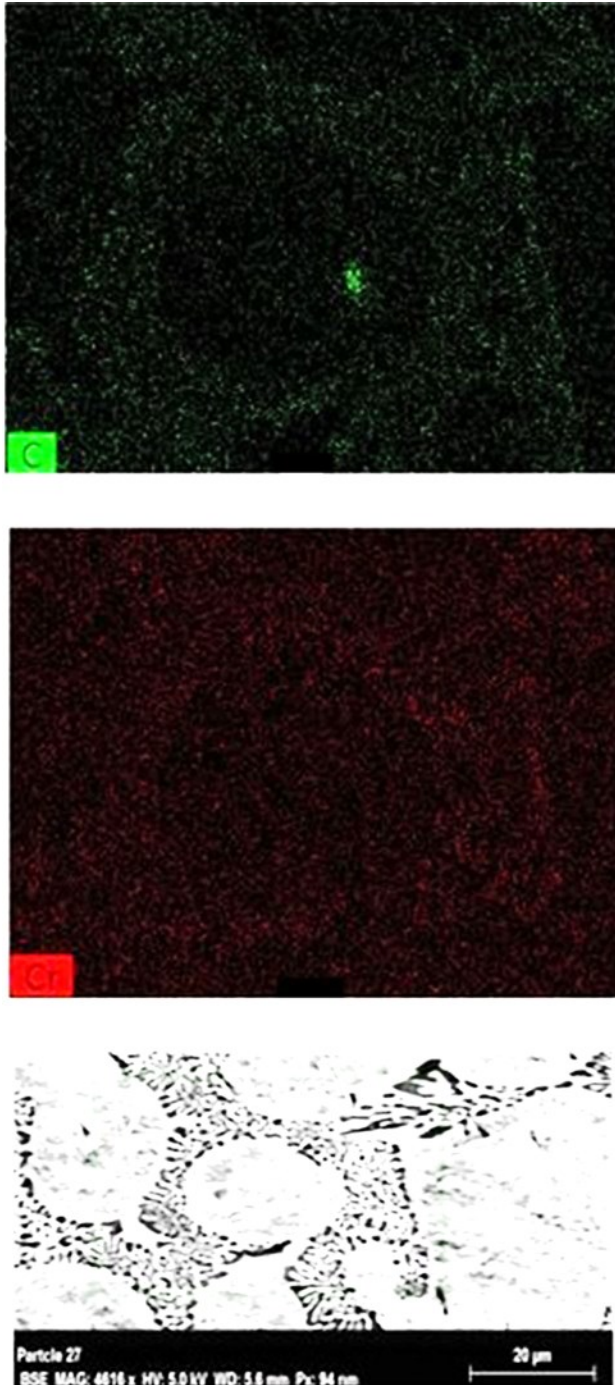


Figure 6-8: EDS elemental mapping of the dendrite

Therefore, variation in elemental distribution brought on by the heterogeneity of dendritic microstructure leads to an increase in chromium content in the inter-dendritic area. However, most of this chromium is in the form of chromium carbides, and as a result, their

creation depletes the free chromium in the inter-dendrite zone, sensitizing the area and eventually lowering the corrosion resistance. Therefore, the behavior of the inter-dendritic corrosion shown by HAZ-1 can be explained by the presence of chromium carbide in the inter-dendritic region. In fact, the literature research [26] links sensitization to declining corrosion resistance in cobalt-based alloys.

CHAPTER 7

INVESTIGATING THE EFFECT OF HEAT TREATMENT ON THE CORROSION RESISTANCE OF STELLITE-6 IN NITRIC ACID ENVIRONMENTS

7.1 Introduction

In industries that produce nitric acid (HNO_3), austenitic stainless steels are used for a variety of components, including pressure vessels, pipelines, and valves. Certain grades of stainless steel, such as 304 and 304L, function admirably over a wide temperature and HNO_3 concentration range. Their corrosion rates at low temperatures at HNO_3 concentrations ranging from 0 to 90% do not exceed 0.13 mm/y [1]. In addition, their corrosion rates remain moderate even at temperatures above the boiling point of HNO_3 so long as HNO_3 concentrations are maintained below 50% [1]. Due to their resistance to corrosion, these materials can be used to manage and store HNO_3 at various temperatures and concentrations [1].

In HNO_3 production facilities, there are numerous valves of various diameters. The gate valve is a common form of valve utilized in these facilities. Typically, a Stellite-6 (ST6) overlay alloy is applied to the interior valve components (gates, discs, guides, and seats) to reduce wear. Previous research (Chapter 6) has demonstrated that the interface zone between the ST6 overlay and stainless steel (304L) substrate is susceptible to corrosion in

nitric acid environments. The study revealed that corrosion occurs primarily in the ST6 overlay's heat affected zone. In addition, it was discovered that HAZ corrosion exhibited an inter-dendritic type and was induced by galvanic corrosion between HAZ and ST6 overlay bulk alloy. Inter-dendritic corrosion and galvanic corrosion were attributed to inhomogeneities in chemical composition and the dilution effect, respectively.

Inhomogeneities in chemical composition and the dilution effect within the microstructure of Stellite alloys have a significant effect on their corrosion resistance [3] [4]. The effect of Stellite alloys' inhomogeneous chemical composition on their corrosion resistance has garnered considerable attention and been extensively studied. When compared to the same Stellite alloys deposited by TIG welding, Wong-Kian et al. [3] reported that the hot isostatically pressed (HIP) casting technique produces a homogenous microstructure, which is reflected in a high erosion-corrosion resistance in a solution containing 5% HNO₃. This result is consistent with the findings of Malayoglu et al.'s [5] study, which determined that corrosion resistance in ST6 with a 3.5% NaCl content generated by the HIPing method was significantly higher than that produced by conventional casting. According to their research, the HIPing method produced spheroidal, uniformly distributed chromium carbides throughout the complete microstructure. In other words, attaining a uniform microstructure within an alloy enhances its corrosion resistance to desirable levels [3] [5].

Researchers examined the effect of dilution on the corrosion resistance of Stellite alloys by focusing on the factors that induce dilution, such as the welding technique and parameters or the thickness of the overlay. It was discovered that dilution has a substantial effect on the corrosion resistance of Stellite alloys. Kim H.-J. et al. [18] investigated the corrosion resistance of ST6 in 3% NaCl superimposed on low carbon steel by Plasma Transfer Arc

(PTA) welding and compared it to the same alloy overlaid by Spray and Fused Open Arc (SFOA) welding. Since the dilution associated with PTA is less than that of the SFOA welding process, the corrosion resistance of ST6 produced by PTA was greater than that of SFOA.

The corrosion resistance of ST6 alloy is inherently determined by two factors. These are the inhomogeneity and dilution of the chemical composition. These two phenomena are diffusion-controlled processes; consequently, if the chemical composition inhomogeneity is improved and the dilution level is decreased, this improvement may alter the alloy's corrosion resistance. However, there are few studies on the effect of heat treating Stellite alloys on their corrosion resistance. In fact, Post Weld Heat Treatment (PWHT) and pre-heating were investigated and found to have no beneficial influence on the corrosion resistance of Stellite-21 welded with GTAW [21]. It was observed that pre-heating at temperatures of 500 °C and 400 °C and PWHT at temperatures of 500 °C and 600 °C were unable to eliminate or reduce the effect of dilution, thereby failing to enhance the corrosion resistance of the investigated alloy. Because it is believed that heat treatment at these temperatures is insufficient to improve corrosion resistance, the influence of different heat treatment regimes (temperature and time) on ST6 corrosion resistance will be investigated in this work. The focus of the study is on correlating the corrosion resistance of ST6 to the metallurgical changes caused by a particular thermal treatment regime. As it was previously demonstrated that the heat-affected zone of ST6 exhibits the lowest corrosion resistance, the corrosion rate will be measured in this zone.

7.2 Results and Discussion

7.2.1 Effect of Heat Treatment on Hardness

Table 7-1, shows the heat treatment temperature and time of the selected specimens. The hardness values of heated-treated specimens were measured to determine the relationship between hardness and heat treatment temperature. ST6 deposited by the GTAW welding process is typically characterized by a hardness range between 380 and 470 HV10 [9], as this alloy is designed with such a high hardness for wear resistance [2]. Lower hardness values of this alloy reduce its wear and abrasion resistance, while higher hardness values can render it completely brittle. Therefore, the hardness value of this alloy must remain within the range specified for its hardness. Therefore, any attempt to improve the corrosion resistance of an alloy through heat treatment must account for the fact that this improvement should not result in scarifying the alloy's specified hardness value.

Figure 7.1 displays the hardness results after thermal treatment. The utilized heat treatment resulted in a discernible difference in hardness among the heat treated specimens. The as-welded specimen (S-1) has a value of 441.2 HV10, which is within the hardness range specified for ST6. Heating at 1200 °C (S-2) drastically decreased the hardness value to approximately 390 HV10. However, this value is still within the hardness range specified for the alloy. When the thermal treatment temperature is decreased below 1200 °C, the hardness values increase significantly. This behavior is evident in the hardness measurements of all specimens from S-3 (1,150 °C) to S-7 (950 °C), where their respective hardness values reached 411 and 469 HV10. After this rise, a tiny drop in the hardness curve reveals a slight decrease in the hardness values corresponding to the S-7 to S-10 specimens. However, it should be noted that none of the heat treatment regimens utilized

in this study caused any specimen to deviate from the hardness range specified for ST6. In summary, the behavior curve for hardness can be divided into four discrete regions. The initial level of hardness as indicated by S-1, followed by a gradual decrease as indicated by S-2, S-3, and S-4. The curve rises again, as in S-5, S-6, and S-7, before falling again in S-8, S-9, and S-10. For the corrosion and metallurgical investigation, a signal specimen representing these four regions (S-1, S-2, S-7, and S-10) will be chosen.

Table 7-1: Heat treatment regimes for the specimens

Specimen	Heat Treatment Temperature (°C)	Soaking Time (hours)
1	As-Welded	2
2	1200	2
3	1150	2
4	1100	2
5	1050	2
6	1000	2
7	950	2
8	900	2
9	850	2
10	800	2

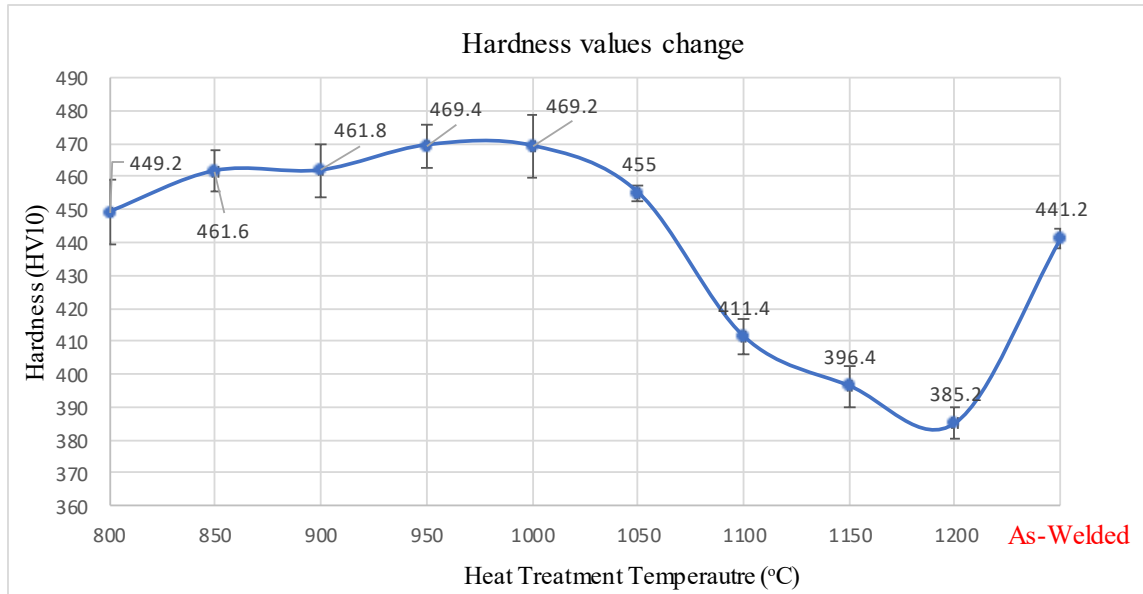


Figure 7-1: Hardness values change with respect to temperature

7.2.2 Effect of Heat Treatment on Corrosion Rate

The corrosion rate of the heat-affected zone of ST6 alloy specimens S-1, S-2, S-7, and S-10 was measured and depicted in Table 7.2 and Figure 7.2. The measurements indicate that the heat treatment had a significant impact on the corrosion rate of the alloy. Comparing S-2 (heated at 1200 °C) to S-1 (as-welded), the former exhibited a significant increase in corrosion resistance, as evidenced by a decrease in corrosion rate from 0.211 mm/y to 0.05 mm/y. This indicates that the S-2 heat treatment regime (1200 °C for two hours) significantly improved the corrosion resistance of ST6 alloy. In contrast, lowering the heat treatment temperature below that caused a detrimental effect on the corrosion resistance of the alloys. Among all specimens tested, S-7 heated at 950 °C exhibited the maximum corrosion rate (1.15 mm/y) at 1.15 m/y. Lastly, heat treatment at 800 °C (S-10) exhibited almost similar behavior to S-7 with a high corrosion rate of 0.624 mm/y.

Table 7-2: Tabulated Corrosion Rate Values of S1, S2, S7 ad S10

Specimen	Heat Treatment Temperature (°C)	Corrosion Rate (mm/year)
S-1	As-Welded	0.211
S-2	1200	0.05
S-7	950	1.15
S-10	800	0.624

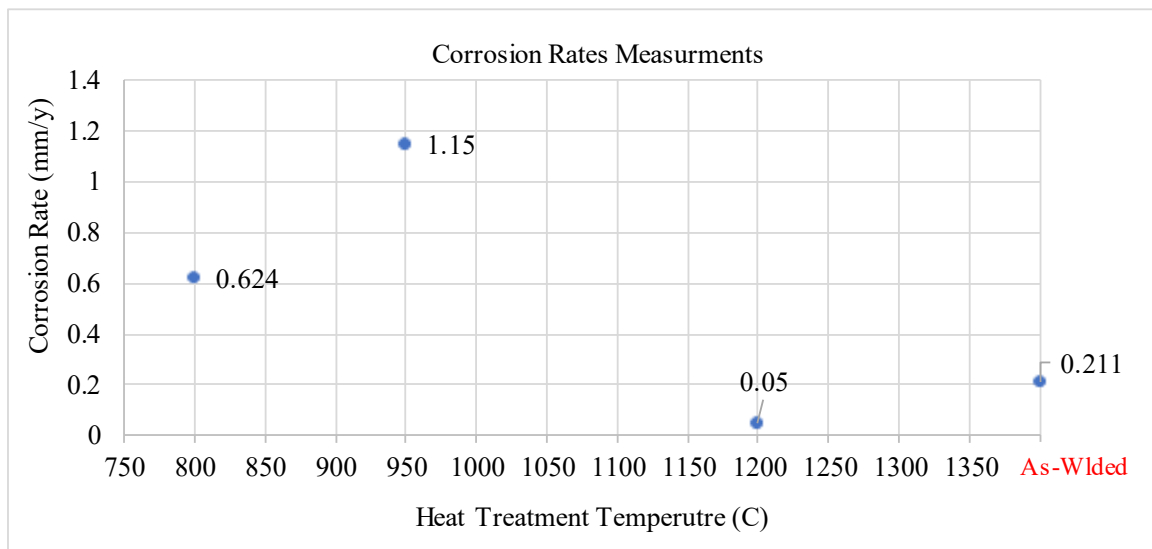


Figure 7-2: Corrosion Rates of S-1,S-2,S-7 and S-10

7.2.3 Effect of Heat Treatment on Microstructure

Figure 7.3 depicts the effect of heat treatment on the microstructure of the alloy as revealed by backscattered SEM of polished specimens. Clearly, each specimen exhibited an entirely distinct morphology, which may account for the difference in corrosion resistance between them. As indicated previously (Chapter 6), the ST6 HAZ displays inter-dendritic corrosion and galvanic corrosion due to inhomogeneous chemical composition and dilution,

respectively. In this work, the effect of heat treatment on the ST6' corrosion resistance will be investigated as a result of altering the level of alloy inhomogeneity and dilution.

7.2.3.1 Chemical Composition Inhomogeneity

S-1(As-welded); The microstructure of S-1 (Figure 7.3(a)) is comprised of four distinct regions with distinctive morphologies. Region 1 represents the matrix of the alloy's dendrite, which is surrounded by region 2, which consists of a relatively coarse lamellae black phase at the boundary of individual dendrites. The third phase (region 3) of this specimen's microstructure consists of a white color morphology phase that is uniformly distributed. In addition, small round black spots (region 4) are visible as part of the microstructure.

Understanding the role of the alloy's different microstructures on its corrosion resistance requires the identification of the phases present in the given microstructure. Figure 7.4 displays XRD peaks that correspond to γ -Co rich phase and other types of carbides, such as $M_{23}C_7$ and MC_6 . According to the elemental mapping depicted in Figure 7.5, region 1 consists primarily of Co-rich phase, which corresponds to the principal component of ST6 alloy. Region 2 demonstrates a high concentration of Cr and C, indicating that the observed lamellae phase is composed of chromium carbide. In addition, this region also contains manganese carbide at a lower concentration, as indicated by the mapping results. Regions 3 of the Wight phase are composed primarily of W and Si (Figure 7.6), while regions 4 are composed of Mo (Figure 7.7). This is consistent with Mirshekari et al's [25] analysis, which identified the observed phases in ST6 alloy as chromium carbide, tungsten carbide, and molybdenum carbide.

It is well known that during solidification, diffusion of the constituent elements and segregation of liquid from the fluid result in an inhomogeneous distribution of the constituent elements within a dendritic matrix [10]. Particularly when chromium carbide precipitates in the form of coarse lamellae morphology as opposed to fine or spheroidal morphology, it is believed that chemical composition inhomogeneity occurs at a high level. Numerous researchers have investigated the inhomogeneity in Stellite alloys from the perspective that it results from the use of various casting or welding techniques during overlay applications. Wong-Kian et al. [3] discovered that the hot Isostatically Pressed (HIP) casting technique produces a more uniform microstructure in Stellite-1, 6, 12, and 21 than the TIG welding procedure. HIPing was discovered to generate fine/spheroidal, uniformly dispersed chromium carbides throughout the entire microstructure, whereas TIG welding produced a coarse lamellae chromium carbide precipitate. Moreover, Malayoglu and colleagues [5] reported that the HIPing casting process generates a homogeneous microstructure (fine spheroidal chromium carbide) in ST6 microstructure when compared to the conventional casting method. In acidic environments, the alloy with coarse lamellae chromium carbide exhibited reduced corrosion resistance than the alloy with fine spheroidal chromium carbide.

In accordance with these analyses, the comparatively high corrosion rate exhibited by S-1 is associated with the presence of coarse lamellae chromium carbide precipitated in the inter-dendritic regions. As it precipitates in this morphology, the distribution of chromium element within the microstructure becomes inhomogeneous. In turn, this inhomogeneity causes certain sites within the microstructure (inter-dendritic boundaries) to have low chromium concentration, or in other words, to be chromium-depleted (sensitized).

Consequently, these sites will have a low corrosion resistance, which will contribute to the observed inter-dendritic corrosion in S-1. Considering that chromium is the primary element that provides corrosion resistance in a nitric acid environment, it is well known and widely accepted that chromium depletion reduces corrosion resistance in this environment [26].

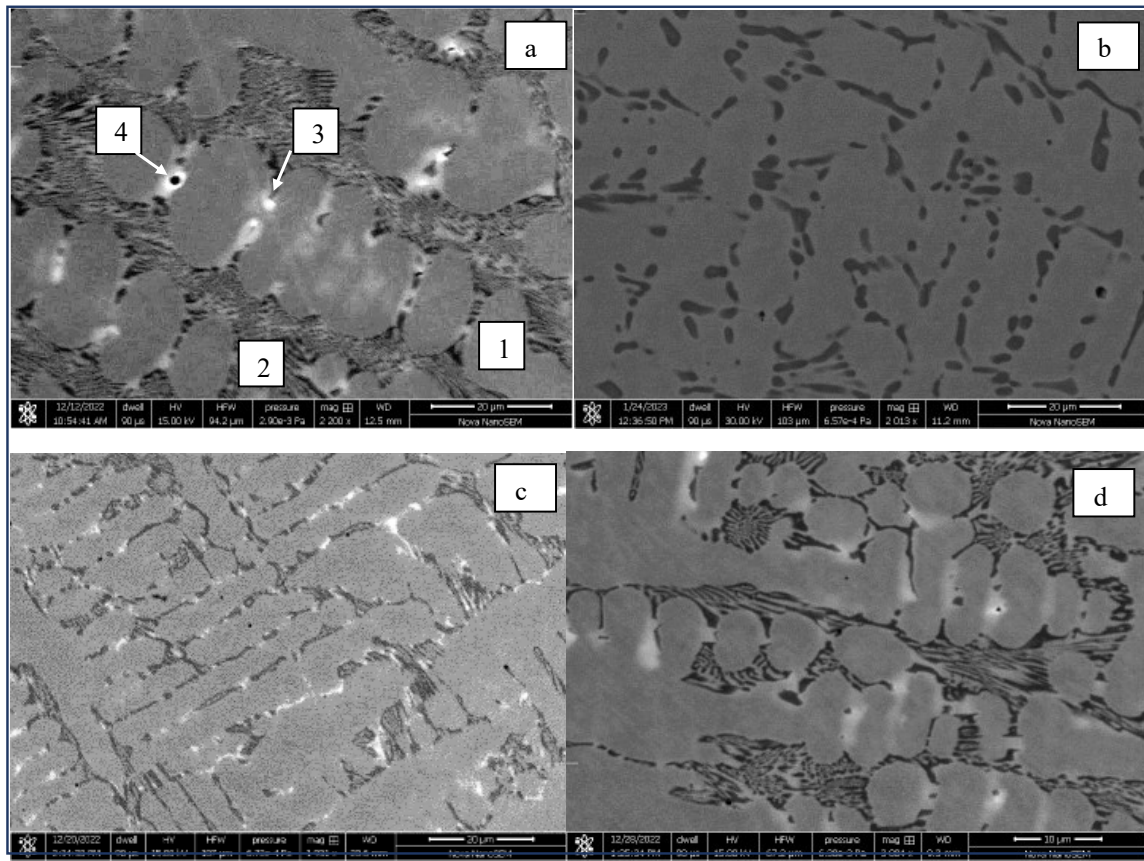


Figure 7-3: Backscattered SEM images for (a) S-1, (b) S-2, (c) S-7 and (d) S-10

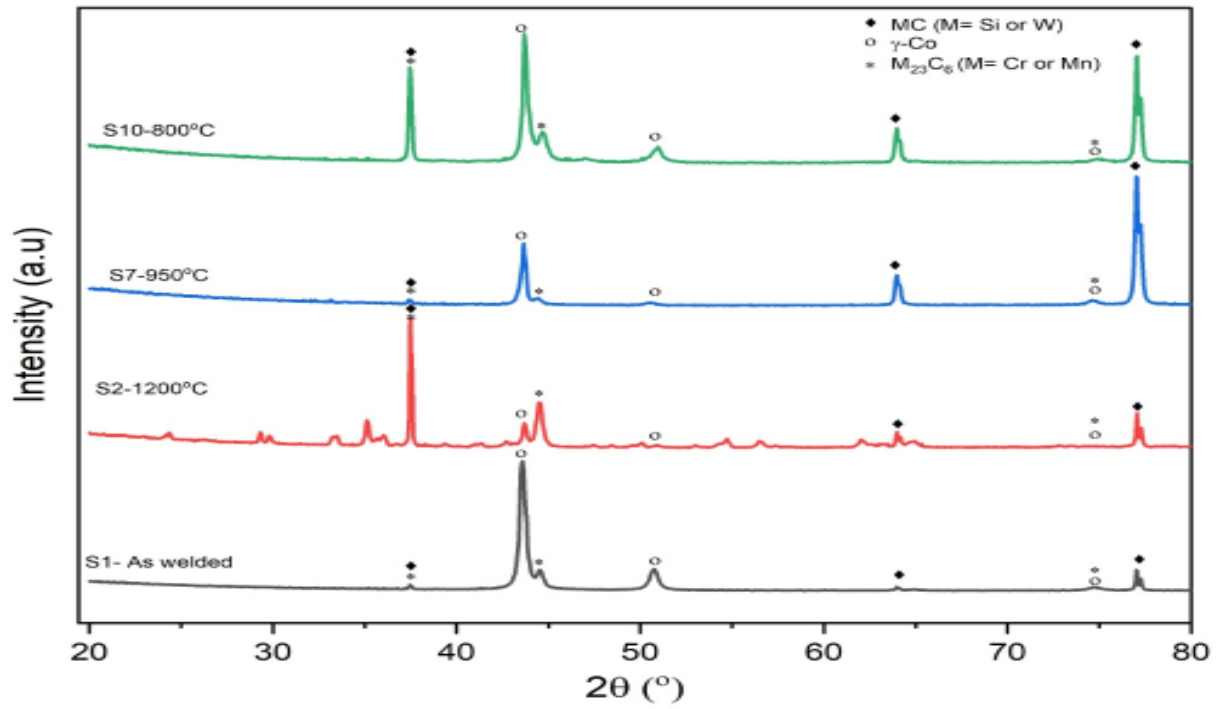


Figure 7-4: XRD results for S-1, S-2, S-7 and S-10 specimens

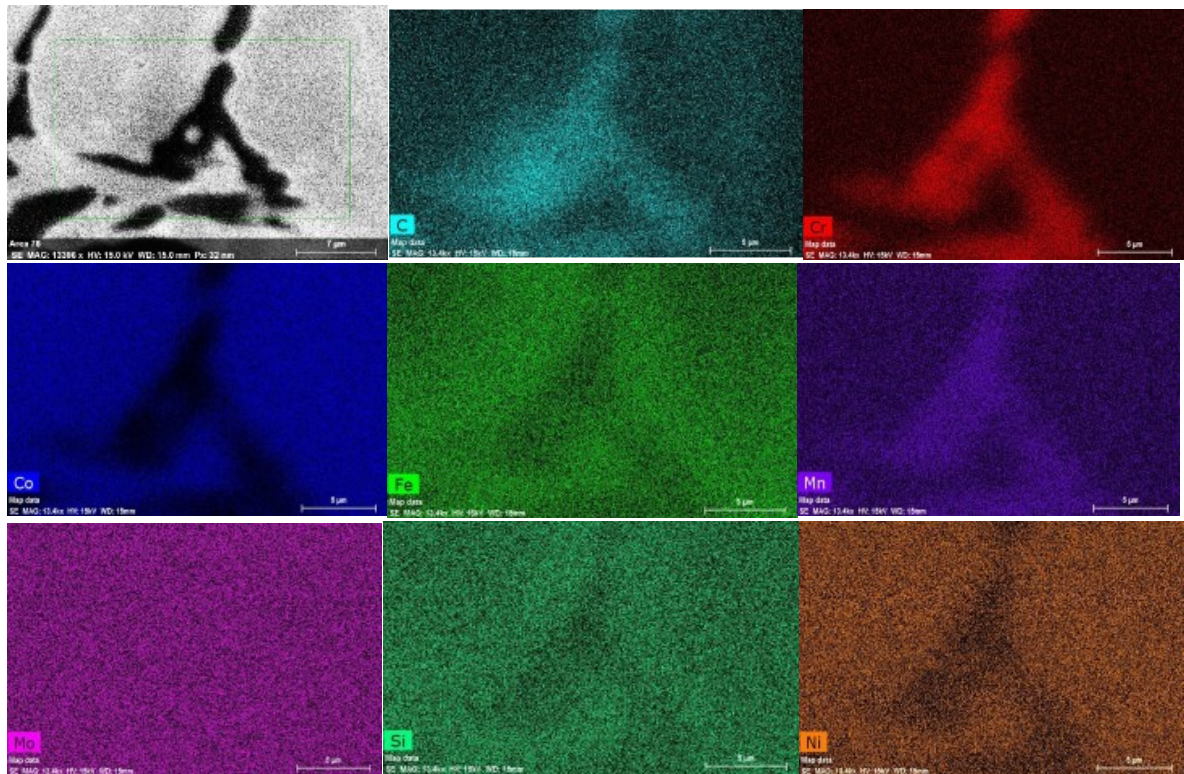


Figure 7-5: Elemental mapping EDS for S-1 specimen showing chromium and manganese carbides

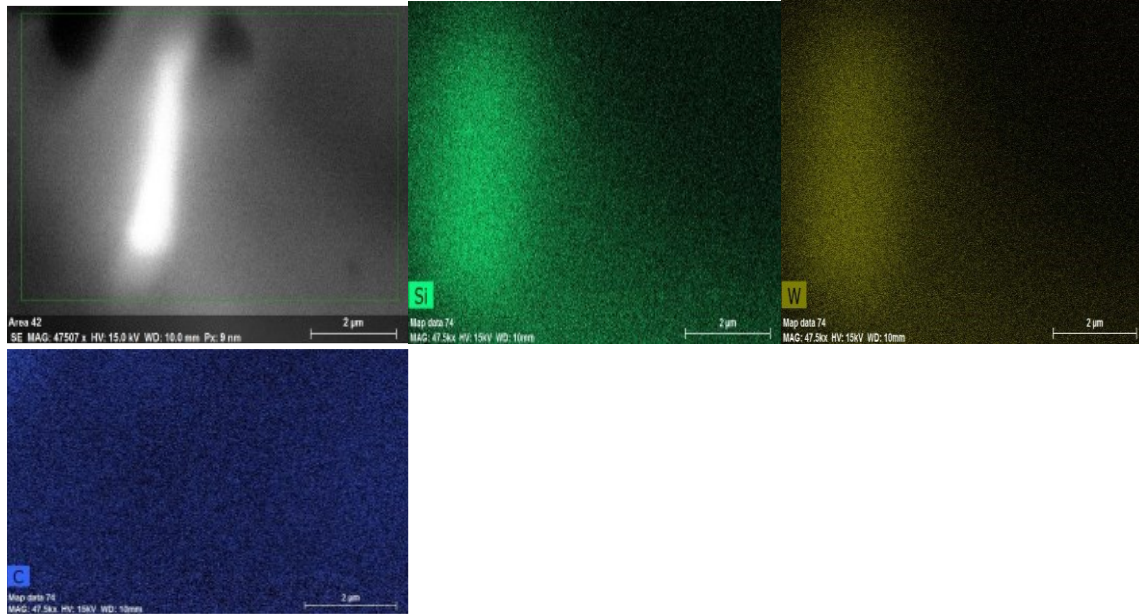


Figure 7-6: Elemental mapping EDS for S-1 specimen showing silicon and tungsten carbides

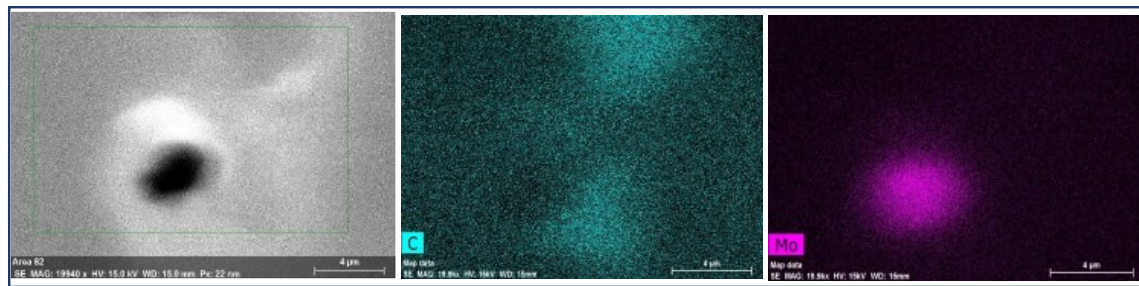


Figure 7-7: Elemental mapping EDS for S-1 specimen showing molybdenum carbides

S-2 (Heat at 1200 °C); Figure 7.3(b) demonstrates that heat treatment at this temperature caused a significant change in the morphology of the microstructure of the alloy. It can be seen that region 2 shrunk in size and transformed into narrow islands and a spheroidal morphology rather than a typical lamella. EDS elemental mapping (Figure 7.8) revealed the presence of chromium and manganese carbides which is comparable in chemical composition to that of S-1. Thus, heat treating the ST6 alloy at 1200 °C for two hours altered the carbides' morphology but not their chemical composition. In fact, the reduction in chromium carbide volume in S-2, decreased the inhomogeneity in the microstructure, allowing for a more uniform distribution of free chromium within the microstructure to be

achieved. Consequently, the developed homogeneity explains the improvement in corrosion resistance observed in specimen S-2, which demonstrates the lowest corrosion rate measurement among the other specimens.

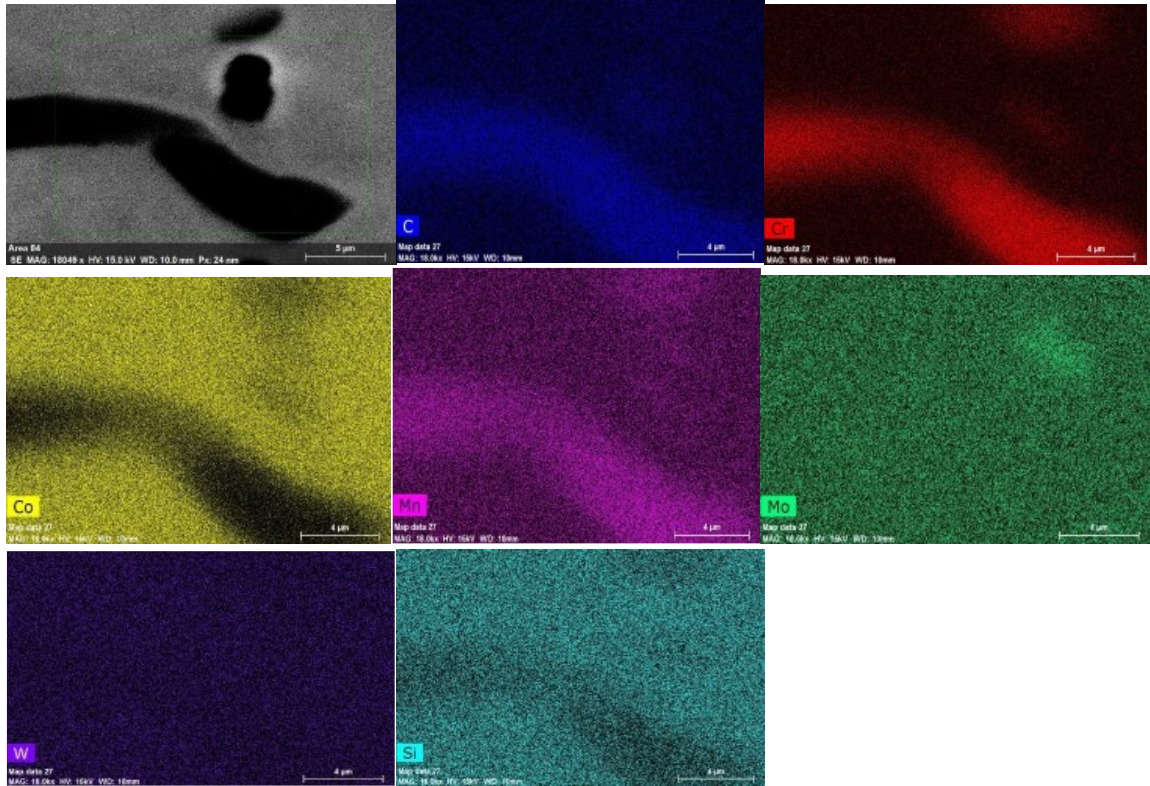


Figure 7-8: Elemental mapping EDS for S-2 specimen showing chromium and manganese carbides

Worth noting, Figure 7.3(b) revealed an observable absence of tungsten and silicon carbides (Region 3) in S-2, indicating that these carbides were dissolved by the heat treatment employed. The absence of these carbides, which are known to decrease the alloy's hardness [7], can explain the decrease in hardness values observed in S-2 in particular.

S-7 (Heat at 950 °C)/S-10(Heated at 800 °C); These specimens exhibited the highest corrosion rate and the greatest hardness values. Figure 7.3(a) and (b), demonstrates that the

morphology of region 2 has not changed significantly compared with S-1. The sites that contain chromium and manganese carbides have the typical morphology of coarse lamellae type. EDS elemental mapping (Figures 7.9 and 7.10) confirmed the presence of chromium and manganese carbides in this region. As stated, the coarse lamellae carbides cause chromium inhomogeneity and thus contribute to the specimens' low corrosion resistance (high corrosion rate). In addition, Figure 7.3(c) and (d), reveal a notable increase in region 3 (silicon and tungsten carbides). The growth of silicon carbide in particular within the dendrite boundaries indicates that the heat treatment at these temperatures forced silicon to segregate into these zones. Increase in silicon in the dendrite boundary has a deleterious effect on corrosion resistance in oxidizing environments [26]. T. Honda and co-workers stated that silicon segregates at the grain boundaries for alloys containing silicon and intergranular corrosion occurs due to the formation of galvanic couples between the boundaries and the matrix within an alloy in the Coriou (8N-HNO₃) and Huey (65 %-NHO₃) solution [27]

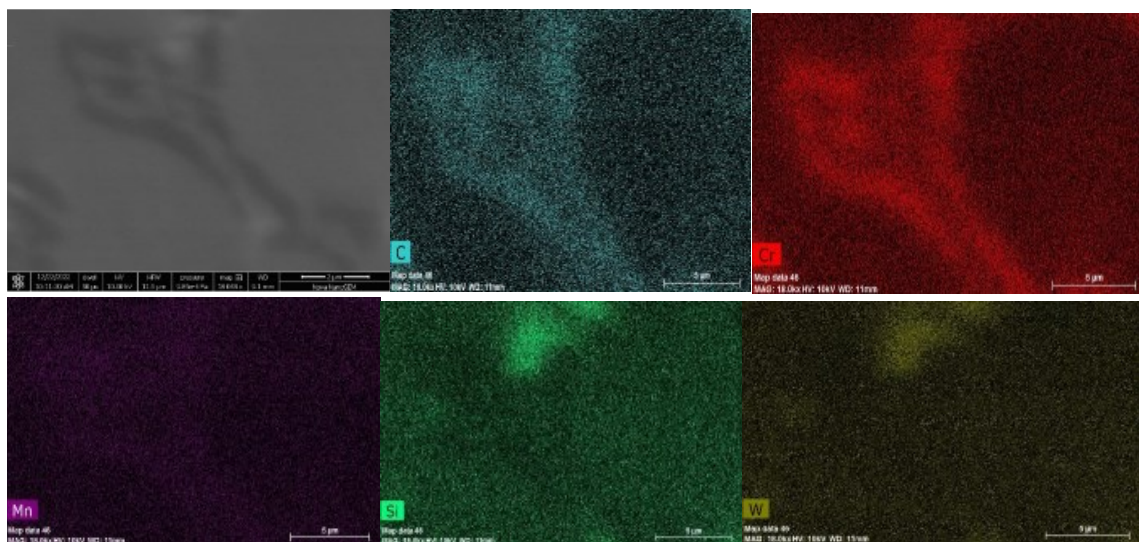


Figure 7-9: Elemental mapping EDS for S-7 specimen

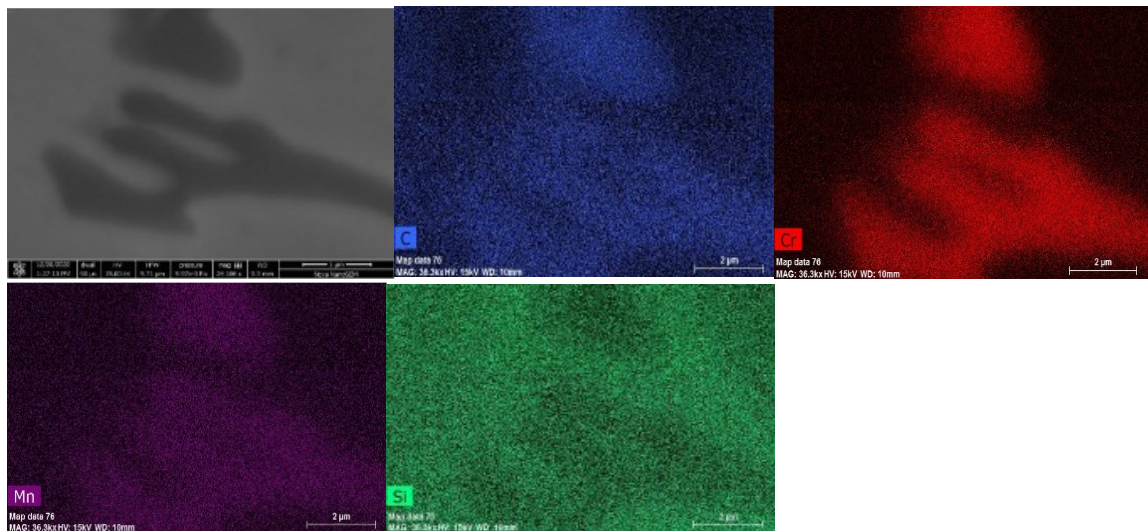


Figure 7-10: Elemental mapping EDS for S-10 specimen

7.2.3.2 Effect of Heat Treatment on Dilution

As indicated previously (Chapter 6), dilution was the primary cause of ST6 HAZ's galvanic corrosion with respect to the bulk of the overlay alloy. Researchers were very interested in the effect of dilution on corrosion resistance, and they were able to establish a reasonable correlation between corrosion severity and dilution levels. With this agreement, it is established that corrosion resistance is inversely proportional to dilution levels. However, researchers focused on reducing the dilution leaves by reducing the heat input during the application of the overlay. Either by regulating a specific welding/casting parameter or by employing a different welding/casting process that can provide the necessary heat input, lower levels of dilution were attained.

Since the purpose of this study is to evaluate the effect of heat treatment on the corrosion resistance of ST6, the change in dilution levels associated with each heat treatment regime was investigated. EDS line scan was applied across the interface zones in order to compare

the dilution levels of each specimen. Chromium was chosen to be scanned in particular because it is the essential element of the corrosion resistance in nitric acid environment.

The EDS line scanning (Figure 7.11(a)) plainly demonstrates that S-1 was diluted in HAZ-1, as the concentration of chromium (moving from the ST6 side towards the substrate) does not drop sharply. In addition, the chromium concentration curve shows a clear plateau at HAZ-1. Thus, the presence of this plateau in HAZ-1 gives an indication for the development of a chromium concentration gradient between HAZ-1 and the ST6 overlay bulk alloy, resulting in galvanic corrosion between these two zones.

In contrast, there is no plateau in the chromium's concentration curves in the remaining specimens (S-2, S-7, and S-10). Figure 7.11(b), (c), and (d) illustrates that the decrease in chromium content between HAZ-1 and ST6 bulk occurs sharply as moving from ST6 to the substrate alloy. Therefore, there is no chromium concentration gradient capable of causing galvanic corrosion between the HAZ-1 and ST6 bulk alloy. This suggests that the utilized heat treatment regimes were able to reduce the effect of dilution in the interface zone and expressed in terms of the chromium concentration gradient in the HAZ-1.

In order to correlate the corrosion behavior of the examined specimens with the improvement in dilution, the low corrosion rate of S-2 can be attributed to the role of the heat treatment's in lowering the dilution level of HAZ-1. Although the other specimens (S-2, S-7, and S-10) experienced an observable improvement in dilution, they suffered from a severe microstructural inhomogeneity that caused them to corrode at an extremely rapid rate.

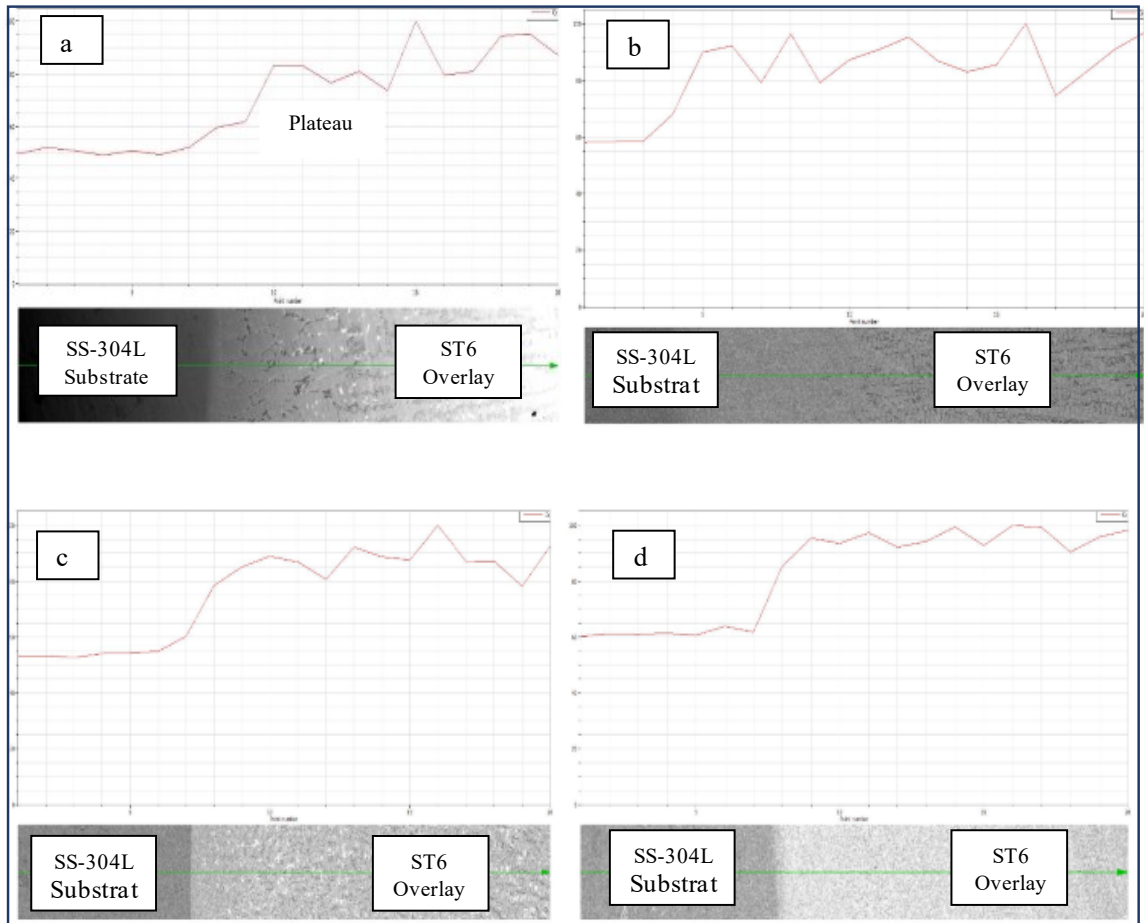


Figure 7-11: EDS line scan across the inter-face zone showing chromium concentration behavior in (a) S-1 specimen, (b) S-2 specimen, (c) S-7 specimen and (d) S-10 specimen

CHAPTER 8

CONCLUSIONS

8.1 General Summary

This study investigates the corrosion defects that occur in stainless steel 304L valves overlaid with Stellite-6 using the GTAW welding process when exposed to 40% HNO₃ at 25 °C. The research revealed that corrosion attacks primarily occur at the interface zone between the substrate and the overlay alloy. The interface zone was distinguished to consist of two distinct heat affected zones corresponding to the heat affected zone of the ST6 alloy (HAZ-1) and the heat affected zone of the stainless steel alloy substrate (HAZ-2). The focus of the investigation was to examine the corrosion mechanisms manifested in the interface zones. The study entails measuring the corrosion rates of samples taken from the overlay, the substrate, and HAZ-1. In this investigation, the corrosion behavior of the examined alloys was correlated with the microstructure morphology of the overlay welding. The possibility of galvanic corrosion between the overlay and HAZ-1 was also investigated. In addition, the study demonstrated that the selection of a particular heat treatment regime can have significant effects on the corrosion behavior of ST6 overlay alloy. Changes in the microstructure's morphology were shown to dictate the alloy's corrosion behavior, which led to the enhancement of the corrosion resistance of HAZ-1. A number of conclusions can be derived from this context:

1. The HAZ-1 that was attached to the Stellite-6 zone exhibited the lowest corrosion resistance due to the dilution effect, which resulted in a considerable drop in the chromium content in the HAZ-1.
2. The HAZ-1 manifests galvanic corrosion behavior by which it acts as an anode with respect to the Stellite-6 overlay.
3. Inhomogeneity in the microstructure of dendrites causes differences in how chromium is distributed. This makes the area between dendrites more sensitive by forming chromium carbide, which causes inter-dendritic corrosion.
4. Heat treating of ST6 at 1200 °C for 2 hours significantly improves the alloys's microstructure homogeneity and dilution which improve it's corrosion resistance consequently.
5. Heat treating of ST6 at 950 °C or 800 °C for 2 hours has a detrimental effect on the corrosion resistance due to the growth of pre-existing silicon carbides that lead to silicon depletion within the microstructure. The silicon depletion further reduces the ST6 corrosion resistance in nitric acid environment.
6. Although all heat treatment regimens used in this study, showed an improvement in the dilution levels among the ST6 HAZ, the microstructure inhomogeneity is the main factor responsible for the undesired corrosion behavior of the specimen's heat treated at 950 °C or 800 °C for 2 hours.

8.2 Recommendations for Future Work

It was shown in this study that a desirable corrosion rate of 0.05 mm/y was achieved by heating the ST6 alloy at 1200 °C. Although this heat treatment regime maintained the required hardness of the alloy, a significant drop in the hardness was observed. Therefore, it is recommended to investigate the corrosion resistance of ST6 in heat treatment temperature range between 1150 °C and 1250 °C. Perhaps this investigation can also obtain a low corrosion rate with a lower drop in the hardness of ST6 alloy.

The corrosion behavior of ST6 was shown in this study to be inherently related to the alloy microstructure morphology. EDS elemental mapping along with XRD analysis were used to identify the ST6 alloy morphology. As these two analysis techniques are considered as relatively qualitative approaches, it is recommended to identify the microstructural phases using Electron Backscatter Diffraction (EBSD) in this regard.

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