UNIVERSITI PUTRA MALAYSIA

PITTING CORROSION RESISTANCE WITH SHIELDED METAL ARC WELDING AND POST WELD HEAT TREATMENT ON DUPLEX STAINLESS STEEL WELD OVERLAY

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By

BERNARD MAXMILLAN SIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

April 2019

DEDICATION

This thesis is dedicated to:

My beloved wife (Sue),

My beloved children (Seraphine, Didymus, Bethany and Stefan),

My beloved parent and parent in law for their patient, encouragement, love, understanding, and support throughout my PhD study.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

PITTING CORROSION RESISTANCE WITH SHIELDED METAL ARC WELDING AND POST WELD HEAT TREATMENT ON DUPLEX STAINLESS STEEL WELD OVERLAY

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BERNARD MAXMILLAN SIM

April 2019

Chair : Associate Professor Tang Sai Hong, PhD
Faculty : Engineering

Duplex stainless steels (DSSs) are widely used in the marine environment, petro-chemical refineries, oil and gas industries because of their high corrosion resistance properties and balanced ratio of austenite and delta-ferrite phases. The objectives of this research are to analyze and evaluate the behavior of pitting corrosion, micro-hardness, microstructure and chemical dilution effects of duplex stainless steel E2209 weld overlay with the hydrogen relief (350°C), stress relief (650°C) and solid solution annealing (1050°C) heat treatments. Shield Metal Arc Welding (SMAW) process with medium heat input produced a reasonable partitioning ratio. The dilution has slightly increased in hydrogen heat treatment and a small reduction for Stress relief heat treatment. Solution annealing with water quenching at above critical point of A3 cooling temperature has shown the disappearance of heat affected zone for low alloy steel substrate. Micro-hardness has indicated a substantial fluctuation of hardness values in fusion zone. The solution annealing has shown a consistent low hardness values at the weld overlay and hardened base metal region with the present of a large amount of maternsite and noticed of equaxied ferrite structures. Ferrite count determination in region of weld metal overlay are increased at hydrogen relief temperatures and decreased at stress relief temperatures due to slow cooling which is more favorable to austenite formation. The amount of ferrite in the weld metals has significantly reduced with the solid solution anneal temperature due to sufficient time for the formation of austenite and giving optimum equilibrium fraction in the welds. The major of alloying elements which can contribute to intermetallic phases are analyzed. C, Cr and Ni chemical elements have shown fluctuation values during PWHT. Whereas, N_2 has produced consistent values to prevent critical implication to nitride precipitation. The corrosion weight loss has gradually increased with the increment of PWHT temperatures. At solid solution annealing temperature, the weld metals are being restored with no significant of weight loss.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KIMPALAN ARKA DAN RAWATAN HABA UNTUK LAPISAN KELULI TAHAN KARAT DUPLEKS TERHADAP KAKISAN PELUBANGAN

Oleh

BERNARD MAXMILLAN SIM

April 2019

Pengerusi : Profesor Madya Tang Sai Hong, PhD
Fakulti : Kejuruteraan

Keluli tahan karat Dupleks (DSS) adalah bahan yang kompleks dengan unsur pengaloi tinggi, bahan-bahan ini telah digunakan secara meluas dalam persekitaran marin, penapisan petro-kimia, industri minyak dan gas kerana nisbah seimbang fasa austenit dan delta-ferit. Objektif penyelidikan ini adalah untuk menganalisis dan menilai tingkah laku kakisan, kekerasan mikro, mikrostruktur dan kesan pengenceran keluli tahan karat keluli tahan karat dupleks E2209 dengan bantuan rawatan haba pelepasan hidrogen pada suhu 350°C, pelepasan tekanan pada suhu 650°C dan pepejal penyelesaian penyepuhlindapan pada suhu 1050°C. Pengenceran telah sedikit meningkat dalam rawatan haba pelepasan hidrogen dan pengurangan kecil untuk rawatan haba pelepasan tekanan. Larutan penyepuhlindapan dengan pelindapkejutan air di atas suhu titik kritikcal A3 telah menunjukkan kehilangan zon terjejas haba untuk substrat keluli aloi rendah. Kekerasan mikro telah menunjukkan perubahan nilai kekerasan yang besar dalam zon campuran. Penyelesaian penyepuhlindapan telah menunjukkan nilai kekerasan rendah yang konsisten pada lapisan kimpalan dan rantaian asas logam yang keras dengan masa kini sejumlah besar tapak matersit dan melihat struktur ferit yang dipersembahkan. Penentuan jumlah ferit di kawasan lapisan logam kimpalan meningkat pada bantuan hidrogen dan menurun pada suhu pelepasan tekanan akibat penyejukan perlahan yang lebih baik kepada austenit pembentukan. Jumlah ferit dalam logam kimpalan berkurang dengan pepejal penyelesaian penyepuhlindapan kerana masa yang mencukupi untuk pembentukan austenit dan memberikan pecahan keseimbangan optimum dalam kimpal. Unsur-unsur aloi utama yang dapat menyumbang kepada fasa intermetallik dianalisis, C, Cr dan Ni unsur kimia telah menunjukkan nilai turun naik semasa rawatan haba kimpalan. N2 telah menghasilkan nilai yang konsisten untuk mencegah implikasi kritikal terhadap pemendakan nitrida. Penurunan berat kakisan meningkat dengan kenaikan suhu pelepasan tekanan. Manakalan pada suhu penyepuhlahan pepejal, logam kimpal dipulihkan tanpa penurunan berat.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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I hereby confirm that:

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LIST OF ABBREVIATIONS

AC	Air Cool
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
AWS	American Welding Society
BM	Base Metal
BSSA	British Stainless Steel Association
Cr_{eq}	Chromium Equivalent
DCEP	Direct Current Electrode Positive
DEP	Shell Design and Engineering Practice
DSS	Duplex Stainless Steel
EDX	Energy Dispersive X-Ray
FN	Ferrite Number
FZ	Fusion Zone
GBA	Grain Boundary Austenite
HAZ	Heat Affected Zone
HI	Heat Input
HV	Vickers Hardness
IGA	Intergranular
IMOA	Institute of Molybdenum Association
Ni_{eq}	Nickel Equivalent
PREN	Pitting Corrosion Resistance Number
PTS	Petronas Technical Standard
PWHT	Post Weld Heat Treatment
SEM	Scanning Electron Microscope
SMAW	Shield Metal Arc Welding
WM	Weld Metal
WA	Widmanstätten
WQ	Water Quench

CHAPTER 1

INTRODUCTION

1.1 Introduction

Duplex stainless steels (DSSs) are complex materials due to high alloying elements, these materials have been widely used in the marine environment, petro-chemical refineries, oil & gas industries, primarily because they offer a better economical for better resistance of pitting corrosion and their ability to maintain good mechanical properties as compared to other stainless steels family (Shamanth & Ravishankar, 2015; Silva et al., 2016). These DSSs are typically manufactured in annealed condition because of their high chromium, molybdenum and nitrogen alloying elements (American Petroleum Institute, 2015), their structures are generally combined with Face Centered Cubit structure (FCC) as austenite (γ) and Body Centered Cubic structure (BCC) as ferrite (α) (Mohammed et al., 2015) as shown in Figure 1.1, although the ratio can vary within 40 to 60% by volume for parent material (API, 2015; Shell and Petronas, 2011).

Most of the marine and offshore components as well as transportation systems such as piping, valves, pumps etc. are commonly used for corrosive internal service media and external hostile conditions especially in chloride environment (Abbas et al., 2015). Therefore, DSSs or their higher grade alloys (Super Duplex) are required for adequate corrosion resistance (Mohammed et al., 2015; Shamanth & Ravishankar, 2015). Pitting corrosion is part of localized corrosion where it attacks chromium oxide locally, normally in the form of spots or pits because of local breakdown of the passive protection layer (Prabhu & Rajnish, 2016). Since pitting corrosion is a part of localized depassivation form of corrosion mechanisms whose “pin holes” or “cavities” are induced in the material’s surface.

The alternative method to improve the material’s pitting corrosion resistance with reliable and affordable cost is using Corrosion Resistant Alloy (CRA) cladding. CRA cladding has been demonstrated to be more cost effective, considering their higher strength, better long-term reliability and light weights (Abbas et al., 2015). The CRA layer is generally obtained by rolling, explosive welding, metallurgical bonding or weld overlaying. Weld overlay is a process whereby one or more metals are fused or jointed to form of complete corrosion resistance alloy protection layer on the surface of substrate material. This weld overlay is chemically bonded to the base metal with a consistent composition alloying element interfaces between the corrosion resistance alloy material and the carbon steel substrate (Abbas et al., 2015). This process approach will allow CRA weld overlay to provide corrosion resistance protection on low alloy carbon steel substrate.

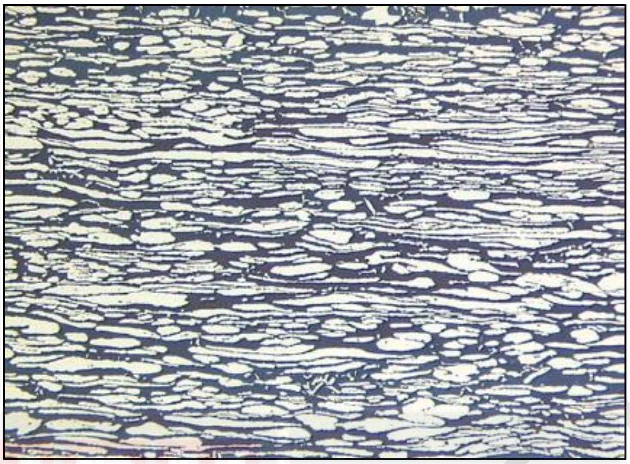

Figure 1.1: Microstructure of duplex stainless steel at x200
(Axel et al., 2015)

In offshore oil and gas fields, most of weld overlay that are cladded on carbon steel pipe materials are generally made by austenitic stainless steels and nickel alloy (Chung et al., 2015; Marques et al., 2015). Duplex CRA weld overlay has not been successfully demonstrated in the oil and gas industries (Petronas, 2012 & 2014) due to some inherent problems in achieving pitting and crevice corrosion resistance caused by intermetallic precipitations which contain Sigma (σ), Chi (χ), chromium and nitride (Cr_2N) are normally presented in fusion zone when at cooling temperature in between 600°C and 1000°C (Sheng et al., 2015; Prabu et al., 2016; Jagesvar et al., 2016). However, Zanotto et al., (2015) have stated that the precipitation and transformation can happen in temperature range of 650°C and 950°C. The formation of sigma phase can severely decrease the ductility and fracture toughness in low temperatures application at -50°C, as well as detrimental the pitting corrosion resistance (Silva et al., 2016).

Furthermore, the balanced phase of DSS is often interrupted during welding, especially by conventional fusion arc welding with high heat energy involved. The influence of heat inputs involved weld parameters (such as ampere, voltage and travel speed) on weld joints are crucial, thus optimization of these parameters during welding becomes essential (Mohammed et al., 2015; Geng et al., 2015). The essential welding parameters to joint DSS welding overlay materials are the thermal cycles (heating, solidification and cooling rates) imposed to the materials that will cause excessive ferritization, unequal/unwanted phases of fusion zone and this leads to deterioration of corrosive resistance and toughness of DSS weldments (Mohammed et al., 2015; Marques et al., 2015; Prabu et al., 2016).

In field welding, PWHT is normally used to decrease residual stresses and reduce the potential of Hydrogen Induced Cold Cracking (HICC), redistribute strains and relieve residual stresses remaining in weld joints and their effects from severe temperature thermal cyclic inherent in welding thermal cyclic (Marques et al., 2015). During welding at high temperature with a sufficient time, the undesirable second phases which can lead to detrimental phase precipitation in DSSs. The precipitation of secondary phases would lower the fracture toughness, ductility and corrosion resistance property. Solution annealing temperatures are normally started from 980°C to 1150°C depending of material grades and their thickness. This process is often followed by rapid cooling to avoid intermetallic formation such as "alpha prime, chi and sigma phases" (IMOA, 2015).

1.2 Problem Statements

Duplex stainless steel obtains an approximately balanced ratio 50:50 distribution of austenite and alpha-ferrite phases, the austenitic phase has a "face-centered cubic" FCC structure and alpha ferrite has a "body-centered cubic" BCC structure. BCC ferrite phase is more susceptible to hydrogen embrittlement as compare to FCC austenite is less susceptible but not always immune. Consequently, duplex stainless steel with combination of ferrite-austenite structure show vulnerable to hydrogen embrittlement and similarly goes to low alloyed steel substrate for duplex weld overlay due to BCC structures.

(a) Post weld heat treatment on DSS weld overlay on low alloy carbon steel substrate is not presented in any industry welding standards. Most of the industrial welding codes industrial welding codes are only covered for individual group of material and dual phase duplex stainless steel materials such as corrosion resistance alloy (CRA) claddings are not well taken care (ASME B31.3, 2016 & ASME VIII, 2017). DSS weld overlays with local PWHT for hydrogen relief and stress relief temperatures have therefore not been critically studied in such details. Consequently, the behavior properties of duplex weld overlays and its materials are less understood. It reveals that at 350°C, the hydrogen degassing temperature has no effect on the DSS cladding; at 650°C, the usual PWHT practiced by industries has major effect on the DSS cladding, inducing the existence of different detrimental intermetallic compounds; and at 1050°C, the austenitizing temperature has totally transformed the dual phases (i.e., α & γ phases) of DSS cladding into the single austenitic (γ) phase as per Fe-C binary phase diagram.

(b) Hardening of the weldment (WM), heat affected zone (HAZ) and base metal (BM) are important because of hydrogen assisted cracking that commonly occurs in low-alloyed carbon steels. As the hardness of the weld metal and HAZ increased, the susceptibility to hydrogen assisted cracking is greater. Higher hardness values obtained is considered unusually indication, therefore PWHT is necessary, regardless of whether it is specified on the welding procedure specification.

(c) There are many research works investigating the resistance of pitting corrosion by using “Polarization Measurement Technique. However, there is insufficient information for pitting corrosion test by using of “Ferric Chloride” Solution in accordance with ASTM G48 Method A. These electrochemical experiments are popular because they are fast compared to weight-loss measurements. Primarily, this method is to distinguish and recognize the reactions, processes, and the stability of the passive film.

(d) Various welding process methods have been utilized for weld overlaying. The selection of welding process and technique are dependent on the conditions such as, accessibility, welding position, alloy type and dilution specified and economical. SMAW is the most basic and common welding process being recognized in all industries, this welding process is relatively simple, low cost and adaptable to any confined space and can be carried out remotely. This welding process also is suitable for out of positions, irregularity shapes of components (eg. Valves, pumps), field repair and high elevation work areas. Excessive dilution by the substrate base metal can cause undesirable chemical and mechanical properties of weld overlay cladding. The multiple layers of overlay are performed to minimize dilution and migration of chemical elements from previous weld pass(s), or provide an intermediate cushion coat to minimize dilution will favorable. Carbon pickup from the low alloyed carbon steel substrate by dilution can contribute the weld overlay more susceptible to hardening transformation to form intermetallic, and may probably result in susceptible to various corrosion attacks, especially pitting corrosion in the weld.

1.3 Aim and Objectives of Thesis

The aim of this research is to study the pitting corrosion and microstructural changes at the interfaces between CRA weld overlay and the low alloyed carbon steel substrate influenced by post weld heat treatments at 350°C 650°C and 1050°C temperatures with air cooled and water quenched methods on duplex stainless steel (DSS) weld overlay for industrial applications.

The research objectives are:-

(a) To determine the corrosion properties and microstructural changes of DSS weld overlay with the influence of PWHT and solid solution annealing treatment.

(b) To analyze the micro hardness of the DSS weld overlay and intermetallic phases subjected different thermal treatments.

(c) To evaluate the microstructure characterization of DSS weld overlay with the impact of hydrogen relief and stress relief, and homogenization thermal treatments.

(d) To study the chemical dilution affecting the distribution active chemical alloying elements at the interfaces between DSS weld overlays and the low alloyed carbon steel substrates.

Table 1.1 Relationship between objectives and problem statements

Objectives	Problem Statements
(a)	(a) & (c)
(b)	(a) & (b)
(c)	(a)
(d)	(a) & (d)

1.4 Scope of Research

Corrosion-resistant weld overlays are often used to reduce the excessive thickness of the substrate, thus to reduce the initial capital costs with CRA weld overlays can improve the service life of components made with an otherwise corrosion-prone material.

This research study is to investigate the impact of the thermal treatments, two (2) series of post weld heat treatment are imposed on standard duplex stainless steel weld overlay (E2209). The initial heat treatment is to provide hydrogen relief condition at 350°C and stress relief at 650°C on the test samples to improve accumulated residual stain caused by thermal cyclic deformation for low alloyed carbon steel material and ensure that duplex weld overlay can maintain its original corrosion resistance properties by performing two different cooling methods (air cool and water quench). The subsequent heat treatment is to reheat the PWHT test samples to solid solution annealing temperature at 1050°C with water quenching, this is to dissolve the secondary phases and transform ferrite to homogenize austenite microstructures.

The mechanical and chemical testing are carried out to verify ferrite volume fraction of an identifiable phase, analysis of dilution and chemical elements distribution, determine the hardness of a material to indentation, metallographic examination to distinguish failures by intermetallic phases, pitting corrosion resistance when test samples are exposed to oxidizing chloride environment and evaluate the physical presence of intermetallic, austenite and ferrite phases.

The limitations of this research are:

a) Post weld heat treatment on DSS weld overlay on low alloy carbon steel substrate is not presented in any industry welding standards. Most of the industrial welding codes are only covered for individual group of material and dual phase duplex stainless steel materials such as corrosion resistance alloy (CRA) cladding are not well taken care.

b) Holding the DSS weld overlay at high recrystallization temperatures encourages grain growth in duplex stainless steel and subsequently cause lack of toughness of the backing material when immediately quenched with water for rapid cooling.

1.5 Thesis Contribution

In petrochemical and oil & gas industries, most of corrosion resistance alloy weld overlay are cladded austenitic stainless steels and high nickel alloys. DSS has demonstrated an extensive mechanical and corrosion properties in chloride environment as compared to other stainless steel grades such as ferritic and austenitic stainless steels. DSS weld overlay by SMAW process has not been successful successfully demonstrated due to some inherent problems in achieving pitting and crevice corrosion resistance caused by intermetallic precipitations presented in heat affected fusion zone.

This research study contributes the outcome of the interrelationship of pitting corrosion, hardness and ferrite contents have been compared with the mandatory requirements of oil & gas industrial engineering practices and also international welding codes. Lower ferrite percentage has been identified and it is confirmed that hydrogen relieving maintains the austenite phase for better corrosion resistance. Solution annealing heat treatments have shown disappearance of heat affected zone and no signification of weight lost in pitting corrosion test.

1.6 Thesis Overview

This thesis consists of introduction, literature review, methodology, results discussion and conclusion:-

Chapter 1 - Contains an introduction to the document, background of studies and addresses the problem statements to the research works. In addition, the scope of research, objectives and list of researchers carried on CRA cladding materials based on journals reviewed are also included in introduction part.

Chapter 2 - The background and literature review, which include the current knowledge theoretical, methodology and findings by other researchers are contributed to relate particular topics will be reviewed. This will enable to identify the gap of analysis to be filled up by proposing other alternative methods used by the industry.

Chapter 3 - An overview of materials, processes and methods are designed for the experimental activities. It explains in the proper sequential order for this research project including preparation, application, testing and collecting critical data of research.

Chapter 4 - All the data are collected, evaluated and analyzed with cross reference to other testing results and reference materials.

Chapter 5 - Conclusion and further recommendation works of this research study are discussed in this chapter.

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BIODATA OF STUDENT

Bernard Sim has graduated with MSc in Welding Engineering from Canfield University, England in 2015. Currently he is attached to Bureau Veritas Malaysia, his roles and responsibilities are managing and coaching industry surveyors to carry out third party inspection and certification against technical delivery and provide support to client on all technical issues relevant to statuary equipment for onshore and offshore oil and gas industries.

He has started to develop the competency skills since year 2003 by attending proficiency training and examination from American Petroleum Institute, Japan Welding Engineering Society, Canada Welding Bureau etc. from Inspector to Senior Engineer levels. He always believes that continuing education opportunities and professional development trainings will enhance or excel the skills, knowledge and experience not only from the professional bodies and also skilled workers.

LIST OF PUBLICATION

Conference Papers

Sim B.M., Tang S.H., Azmah H., Jong E.N.T. and Mahesh T. (2017). The Effect of GTAW Process Welding Parameter on Weld Bead Geometry and Mechanical Properties of 2205 DSS Materials. Submitted to 20th International Conference Advance in Materials & Processing Technologies in Chennai, India, July 2017.

Sim B.M., Tang S.H., Azmah H., Jong E.N.T. and Mahesh T. (2018).The Effects of Heat Treatment on Microstructures and Dilution of SMAW DSS Weld Overlay. Submitted to 21st International Conference Advance in Materials & Processing Technologies in Dublin, Ireland, 2018

Journal Papers

Sim B.M., Tang S.H., Azmah H., Jong E.N.T. and Mahesh T. (2019). The influence of PWHT precipitation on DSS weld overlay towards pitting corrosion. Materials, 20: 3285, https//doi.org/10.3990/ma12203285

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