

Declaration

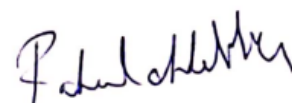
I hereby declare that the work presented in this Thesis titled "*Experimental investigations on dissimilar metal welds for offshore applications*" submitted to the Indian Institute of Technology Jodhpur in partial fulfillment of the requirements for the award of the degree of Doctorate of Philosophy, is a bonafide record of the research work carried out under the supervision of *Dr. Rahul Chhibber*. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.



Waris Nawaz Khan
(P16ME005)

Certificate

This is to certify that the thesis titled *Experimental investigations on dissimilar metal welds for offshore applications* submitted by Waris Nawaz Khan (P16ME005) to the Indian Institute of Technology, Jodhpur for the award of the degree of Doctorate of Philosophy is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the content of this report, in full or in parts, have not been submitted to any other Institute or University in India or abroad for the award of any degree or diploma.



Dr. Rahul Chhibber
IIT Jodhpur
PhD Supervisor

Acknowledgments

The completion of Ph.D. journey is a result of efforts and prayers of many people. I realize no words can do justice to my supervisor Dr. Rahul Chhibber for his guidance, support, and push towards achieving the goals throughout. Dr. Rahul Chhibber made my first introduction to the field of research in welding and joining. The freedom and comfort he offers his students made the days spent in his lab joyful and memorable for me. From the beginning phase of problem formulation to the analysis of results followed by the reviewing of manuscripts, his efforts made my work much easier and streamlined in each stage. His patience, calmness, and understanding of problems are some lessons that will stay with me forever. I hope and look forward to always have the blessings of his guidance in the career path that awaits me after Ph.D.

I sincerely appreciate the help from the Department of Mechanical Engineering, IIT Jodhpur, laboratory staff of Central Workshop, Center for Advanced Scientific Equipment (CASE), and Office of Academics for their assistance rendered in different capacities to carry out the work with much ease and reduced efforts. I am also thankful to Science & Engineering Research Board (SERB), Govt. of India for the award of SERB-OVDF 2019 providing me an opportunity to carry out a part of thesis work at the University of Alberta, Canada.

I profoundly acknowledge the mentorship of Prof. Leijun Li, Department of Chemical & Materials Engineering at the University of Alberta, Canada. Prof. Li hosted me under the SERB-Overseas Visiting Doctoral Fellowship, which turned out an amazing learning experience. His scientific approach and insightful discussions helped in bringing out some meaningful and interesting results reported in this thesis. A much thanks to all the members of Prof Li's research group, for helping me adapt in the new place, assisting in research work, and making my stay in Canada full of good memories.

I would also appreciate family like atmosphere in the lab at IIT Jodhpur from my labmates Dr. Rakesh Joshi, Dr. Lochan Sharma, Dr. Sumit Mahajan, and Furkan. Our weekly dine outs and endless tea time discussions were enough to take away stress from work and personal life. The current lab members Anup, Aditya, and Vijay made the brotherhood go strong and helped whenever asked for.

I derived the biggest source of energy for the completion of this work from my family. I have grown up seeing my parent prioritizing and sacrificing a lot to fulfill their dream of giving me the best of education. Their efforts, blessing, and prayers enabled me to complete this thesis with utmost honesty and dedication. My mother has been my biggest source of strength and unconditional love throughout my life, and none of this was possible without her always being on my side. She always supported my choice, dreams and took pride in even my smallest achievement. This Ph.D. is a dream of my father, a man of hard work and dedication who in his limited resources, always managed financial responsibilities, to keep me focused on the studies. Life lessons from my father showed me the way to keep going on this Ph.D. journey firmly and patiently. A small talk with my brother (Wali), sister (Mazia), and my cute niece (Hooriyah) was enough to refresh me to do away all worries of the day and remain in the best state of mind.

In the end, and most importantly, I offer my thanks to Almighty Allah for His divine blessings and kindness towards me. As written, 'He honor whom He please and abase whom He please.' I thank Allah for all that He has blessed me with and for all that He saved me from in this life.

List of Figures

Figure	Title	Page
1.1	Investment in exploration and production activities 2015-19	1
1.2	Examples of offshore structures	2
1.3	Material selection tree	2
2.1	Types of offshore structures	8
2.2	Different zones in offshore structures	9
2.3	Development of different grades of pipeline steel from 1990 onwards	9
2.4	Microstructure of X52 pipeline steel	12
2.5	Microstructure of super duplex stainless steel	14
2.6	Phase diagram of super duplex stainless steel solidifying with different γ and δ proportion	14
2.7	TTT diagram for super duplex stainless steel	15
2.8	Microstructure of duplex and super duplex stainless steel after treating for 1 hour at 850°C: A, B- Glyceregia reagent, C,D- Grosbeck's reagent, E,F- Murakami (modified) reagent	16
2.9	Sigma phase and cracks: (a) Two macro-scale cracks (b) Crack 1 surrounded by macro-scale cracks (c) Blocky σ with cracks (d) Coral σ with cracks	16
2.10	EBSD (a, c, e, g) and Inverse Pole Figure (IPF) maps (b, d, f, h) of σ precipitation at different temperatures along with the change in morphology from blocky to coral shaped	17
2.11	Weld microstructure obtained from different welding processes: (a) Weld bead EBW (b) Microstructure EBW (c) Hybrid weld bead (d) Microstructure with different cooling rate and ferrite content (e) GMAW weld (f) Hybrid PAW weld (g) PAW weld (h) Hybrid (laser + GMA) weld bead (i) Weld microstructure at different sections (j) Hybrid (laser+MIG) weld	20
2.12	Microstructure of multi pass super duplex stainless weld	20
2.13	Protection methods suggested by MPI	21
2.14	Representation of the SMAW process	22
2.15	Weld metal chemistry and properties	24
2.16	Schematic representation of the GTAW process	25
2.17	Constitutional diagrams	26
2.18	Effect of heat input on 2507/X65 GTA weld	27
2.19	GTA weld zone microstructure: (a) ER2594 filler (b) ER309LMo filler	28
2.20	Comparison of SMAW 2205/X52 fabricated using ER2209 and ER309L	28
3.1	Work Plan	32
4.1	Design space for 'k' ingredients	34
4.2	Ternary phase diagram	37
4.3	Design space diagram	37
4.4	Electrode extrusion process	37
4.5	Wettability parameters	39
4.6	Weld joint design	40
4.7	Schematic representation of characterization specimens	42
5.1	Schematic of SMAW electrode development	44
5.2	Density of coating compositions	46
5.3	Heat flow curve for enthalpy calculation	46
5.4	Types of melting and spreading patterns: (a) Complete melting (b) Partial Melting	47
5.5	Predicted versus Actual plots for physicochemical-thermophysical properties	52
5.6	Predicted versus Actual plots for wettability properties	52
5.7	Contour plots for physicochemical-thermophysical properties	53

5.8	Contour plots for wettability properties	53
5.9	XRD and FTIR plots of electrode coating	54
5.10	Thermal properties of red ochre	55
5.11	Weight loss and enthalpy of red ochre	55
5.12	BET surface analysis plot of red ochre	56
5.13	Structural characterization of red ochre	56
5.14	Schematic of multi pass bead on plate experiment	57
5.15	Multi pass bead made using laboratory developed electrodes	57
5.16	Microstructure of multi pass beads applied using laboratory developed Electrode 21	58
5.17	Dilution for multi pass beads on plate applied using laboratory developed: (a) Electrode 3 (b) Electrode 21	58
5.18	Microhardness plot for multi-pass weld beads	59
5.19	Predicted versus Actual plots for weld bead chemistry and properties	62
5.20	Contour plots for bead properties	64
5.21	Contour plots of optimum solutions' desirability	66
5.22	Schematic of SMAW weld fabrication and characterization	68
5.23	SMAW weld geometry and characterization plan	68
5.24	Macrograph of weld deposition	69
5.25	Fractured tensile specimen of SMA welds	70
5.26	Fractograph of weld tensile specimens	70
5.27	Fractured surface appearance of an impact specimen	71
5.28	Microhardness profile of welds	72
5.29	Schematic for metallurgical characterization of SMA welds	72
5.30	Microstructure of base metals: (a) API X70 (b) Super duplex stainless steel 2507	73
5.31	XRD of base metal	73
5.32	Fe-Cr-Ni pseudo binary diagram and Schaeffler diagram plot for the 309L filler and welds	73
5.33	Microstructure of weld fusion zone	74
5.34	Microstructure of heat affected zone on X70 side	75
5.35	Microstructure of heat affected zone on super duplex side	75
5.36	Elemental composition in different zones of dissimilar weld made using E309L	76
5.37	Solidification cracking susceptibility of welds based on (P+S wt. %)	77
5.38	Scheil solidification calculation for SMAW welds	78
5.39	Equilibrium phase estimation using ThermoCalc for the SMAW weld made using electrodes: (a) E309L (b) E16 (c) E21	79
5.40	Schematic of SMAW weld's wear and corrosion characterization	79
5.41	Wear results for the SMAW welds	80
5.42	Wear mechanism	80
5.43	Tafel plots for base metals and SMAW process made welds	81
5.44	Schematic of weld fabrication using GTAW and characterization	82
5.45	GTAW weld geometry and characterization plan	82
5.46	Macrograph of weld deposition	83
5.47	Fe-Cr-Ni pseudo binary diagram for general solidification mode of filler metals	84
5.48	Cracking susceptibility for solidification mode of filler metals	84
5.49	Precipitation of reformed austenites in super duplex filler weld	84
5.50	Microstructure of weld fusion zone for filler metal SDSS 2594	85
5.51	Microstructure of weld fusion zone for filler metal ASS 309L	86
5.52	Microstructure in different sections of GTA weld	86
5.53	XRD of weld fusion zone for filler metals: (a) ASS 309L (b) SDSS 2594	87
5.54	Calculations of Scheil solidification: (a) Weld by 2594 filler (b) Weld by 309L filler	87
5.55	Equilibrium phase calculation for the 309L filler weld using ThermoCalc	88
5.56	Equilibrium phase calculation for the 2594 filler weld using ThermoCalc	88
5.57	Heat affected zone on X70 side	89
5.58	HAZ on super duplex side for welds with: (a) super duplex 2594 filler metal (b) austenitic 309L filler metal	90
5.59	Schaeffler diagram for predicting microstructure	90
5.60	WRC-1992 and Schaeffler diagram for weld	91
5.61	Fractograph of tensile specimen	92

5.62	Microhardness profile of welds	93
5.63	Schematic of corrosion investigation	94
5.64	Tafel plot for different zones of dissimilar welds: (a) Base metals (b) Weld zone (c) HAZ on X70 side (d) HAZ on SDSS side	94
5.65	Grain boundary angle and KAM in weld fusion zones	95
5.66	Distribution of average diameters of δ and γ grains in the weld zones	96
5.67	Grain boundary angle in heat affected zone	97
5.68	Elemental analysis at X70/Weld interphase	97
5.69	Pitting in heat affected zone on X70 side	98
5.70	TTT diagram of a duplex stainless steel	98
5.71	Wear property characteristics in dry sliding wear	100
5.72	Wear with time in dry sliding wear test	101
5.73	Comparison of wear parameters (a) Volume Loss (b) Wear Rate (c) Specific Wear Coefficient	101
5.74	Comparison of Wear in NaCl and HCl medium	102
5.75	Friction force acting on pin specimen in the environment of 3.5% NaCl solution	103
5.76	Wear in the environment of 3.5% NaCl solution	103
5.77	Weight Loss with changing sliding distance for specimen: (a) As Received (b) 700-20 (c) 475-180 (d) 875-180	104
5.78	Progressive wear with increasing sliding distance in 1M HCl solution	104
5.79	Wear mechanism	105
5.80	Corroded specimens in 3.5% NaCl solution (a) X70 steel (b) As Received SDSS (c) 875-180 SDSS	106
5.81	Corroded specimens in artificial ocean water: (a) X70 steel (b) As Received SDSS (c) 875-180 SDSS	106

List of Tables

Table	Title	Page
1.1	Corrosion resistant alloys for offshore application	3
2.1	Marine location and property	8
2.2	Chemical composition of API pipeline steel recent grades (wt. %)	10
2.3	PREN values of different grades of stainless steel	13
2.4	Welding processes used for welding pipeline steels	18
2.5	Role of electrode coating constituent minerals	23
4.1	Chemical composition of coating's mineral constituents (wt. %)	33
4.2	Chemical composition of base and filler metals (wt. %)	33
4.3	Coefficient of thermal expansion for base and filler metals	34
4.4	Formulated coating composition (wt. %)	35
4.5	Electrode coating compositions	36
4.6	Surface tension factor of constituent minerals	39
4.7	Qualitative observation of trail parameter	39
4.8	Etchants used for microstructure investigations	41
4.9	Mechanical characterization of welds	42
5.1	Design matrix for electrode coating compositions	44
5.2	Characterization of SMAW electrode coating	44
5.3	Thermophysical and physicochemical properties of coatings	45
5.4	Wettability properties of coatings	45
5.5	ANOVA for physicochemical and thermophysical properties	47
5.6	ANOVA for wettability properties	49
5.7	Effect of coating constituents on physicochemical and thermophysical properties	50
5.8	Effect of coating constituents on wettability properties	50
5.9	Model validation for electrode coating properties	54
5.10	Chemical composition of beads (% wt.)	59
5.11	ANOVA for multi pass bead on plate weld chemistry and properties	60
5.12	Effect of coating constituents on physicochemical and thermophysical properties	62
5.13	Model validation for deposited bead properties	64
5.14	Optimum Solution for physicochemical-thermophysical properties	65
5.15	Properties of electrode with optimum solution coatings	66
5.16	Comparative assessment for electrode coating performance	67
5.17	SMAW weld parameters	69
5.18	Tensile properties of welds and base metals	69
5.19	Impact Energy of weld and HAZ (J)	71
5.20	Weld fusion zone chemistry obtained using atomic absorption spectrometer	76
5.21	Dilution calculations	77
5.22	Transformation temperatures calculated using ThermoCalc	78
5.23	Corrosion potential of base metals and welds	81
5.24	GTAW weld parameters	83
5.25	Transformation temperatures calculated using Thermo-calc	87
5.26	Tensile Properties of GTA welds and base metals	92
5.27	Impact Energy of base and weld specimen	93
5.28	Corrosion potential of base metals and welds	94
5.29	Heat treatment conditions	99
5.30	Cleaning solution for cyclic immersion corrosion specimen	105

List of Symbols

Symbol	Description
γ	Austenite
α_p	Pearlitic ferrite
C_p	Cementite
δ	Delta ferrite
α	Alpha ferrite
σ	Sigma phase
χ	Chi phase
$M_{23}C_6$	Metal carbide
α'	Alpha phase
γ_2	Secondary austenite
V_v	Volume fraction
Q	Activation energy
R	Universal gas constant
Cr_{eq}	Chromium equivalent
Ni_{eq}	Nickel equivalent
X_i	Individual constituent in electrode coating
α_i	Lower limit on coating constituent concentration
β_i	Upper limit on coating constituent concentration
k	Number of coating constituents
ρ	Density
m	Mass
V	Volume
γ_{SL}	Interfacial tension at solid/liquid interface
γ_{SG}	Interfacial tension at solid/gas interface
γ_{LG}	Interfacial tension at liquid/gas interface
θ	Contact angle
f_n	Surface tension factor
W_a	Adhesion energy
A	Area
η	Efficiency
V	Potential
I	Current
ΔH	Enthalpy of fusion
ΔW	Change in weight
K	Thermal conductivity
D	Thermal diffusivity
S	Specific heat
dF	Degree of freedom
R	Coefficient of correlation
\dot{A}	Armstrong
P_o/P	Relative pressure

E16	Laboratory developed electrode of coating composition 16
E21	Laboratory developed electrode of coating composition 21
E_{corr}	Corrosion potential
L	Liquid
M	Martensite
PREn	Pitting resistance equivalent number
γ/δ	Austenite/ferrite boundary
Q	Wear rate
H	Hardness
F_N	Normal force
Ks	Specific wear constant
CR	Corrosion rate
T	Time of exposure

List of Abbreviations

Abbreviation	Full form
FPSO	Floating Production Storage and Offloading
API	American Petroleum Industry
SMAW	Shielded Metal Arc Welding
GMAW	Gas Metal Arc Welding
GTAW	Gas Tungsten Arc Welding
SAW	Submerged Arc Welding
HAZ	Heat Affected Zone
ACC	Accelerated Cooling
TMCP	Thermo Mechanically Controlled Processing
SAF	Sandvik Austenite ferrite
UNS	Unified Numbering System
SDSS	Super Duplex Stainless Steel
TTT	Time Temperature Transformation
IPF	Inverse Pole Figure
EBSD	Electron Backscatter Diffraction
CE	Carbon Equivalent
FSW	Friction Stir Weld
PAW	Plasma Arc Welding
FCAW	Flux Core Arc Welding
HT-HAZ	High Temperature- Heat Affected Zone
LT-HAZ	Low Temperature- Heat Affected Zone
DCEP	Direct Current Electrode Positive
DCEN	Direct Current Electrode Negative
ER	Electrode Rod
GBA	Grain Boundary Austenite
WA	Widmanstätten Austenite
PTA	Partially Transformed Austenite
IGA	Inter Granular Austenite
ANOVA	Analysis of Variance
HT	Heat Treated
M/A	Martensite/Austenite
F-A	Ferrite Austenite
F	Ferrite
A	Austenite
HAGBs	High Angle Grain Boundaries
LAGBs	Low Angle Grain Boundaries
KAM	Kernel Average Misorientation