

This chapter presents the findings of experimental investigations carried out in this work, along with the discussion of the results to obtain meaningful interpretation of quantitative and qualitative characterization.

5.1. FORMULATION AND CHARACTERIZATION OF SMAW ELECTRODE COATINGS

The coated electrodes used in SMAW process are important for ensuring the produced weld has desirable properties. Selection of mineral constituents for electrode coating is of utmost importance, as they individually and their interactions combined, influence the electrode behavior significantly. The design and development of coated electrodes starts from choosing the desired basicity range of electrode coating, based on which the mineral constituents and their composition is decided from their respective ternary phase diagrams. The coating composition is then tested for various properties and upon satisfactory results; it is extruded on a filler wire for the fabrication of electrodes. The fabricated electrodes are used to make multi-pass beads on plate whose qualitative and quantitative characterization helps us to choose the most suitable coating compositions. These chosen most suitable coating compositions and a commercial grade coated electrode of same filler wire is then used to fabricate weld between our materials of interest, i.e. super duplex stainless steel 2507, and pipeline steel API X70. Mechanical and metallurgical characterizations of fabricated welds help us to assess the performance behavior of our laboratory developed electrode coating. The ternary phase diagram and corresponding design matrix developed using the mixture design approach has already been discussed previously in Chapter 4. This section further discusses a sequential methodology to develop SMAW electrodes for fabricating an offshore structure weld between super duplex stainless steel 2507 and pipeline steel API X70.

5.1.1. CHARACTERIZATION OF ELECTRODE COATINGS

The electrode coatings were formulated as per the design matrix presented in Table 5.1. The developed electrode coating compositions were characterized for different properties as given in the Table 5.2. A schematic of electrode coating characterization is provided in Figure 5.1.

Table 5.1: Design matrix for electrode coating compositions

Coating	CaO	CaF ₂	TiO ₂	SiO ₂	Red Ochre
1	30	25	25	10	5
2	35	20	25	10	5
3	35	25	20	10	5
4	32	25	27.5	5	5
5	31.5	21.25	30	7.5	5
6	25	25	30	10	5
7	32.5	22.5	27.5	7.5	5
8	35	17.5	30	7.5	5
9	35	25	25	5	5
10	35	21.2	26.2	7.5	5
11	33.3	23.3	28.3	5	5
12	30	25	30	5	5
13	31.6	21.6	26.6	10	5
14	31.25	25	26.2	7.5	5
15	35	20	30	5	5
16	35	15	30	10	5
17	32.5	22.5	30	5	5
18	30	20	30	10	5
19	35	22.5	27.5	5	5
20	27.5	25	30	7.5	5
21	35	25	22.5	7.5	5

Table 5.2: Characterization of SMAW electrode coating

S. No	Characterization	Properties
1	Thermophysical & Physicochemical	Enthalpy of fusion, thermal stability, specific heat, conductivity, diffusivity, density,
2	Wettability	Contact angle, surface energy, spread ability
3	Structural	Phases, bond energy

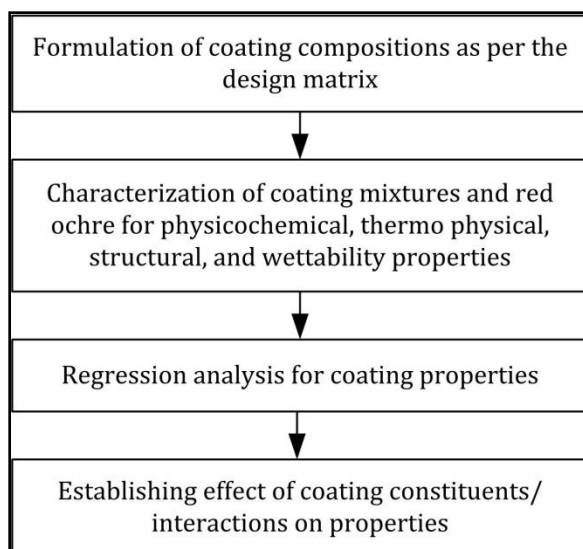


Figure 5.1: Schematic of SMAW electrode development

5.1.2. EXPERIMENTAL RESULTS OF ELECTRODE COATING CHARACTERIZATION

The experimental value of various coating properties is summarized in Table 5.3 and Table 5.4. These properties are an indicator of how the coating will perform when extruded on the core wire. Most of the properties are temperature dependent and have been tested at varying temperature ranges. Figure 5.2-5.3 shows the representative plots of density, and heat flow curve used to calculate enthalpy for different electrode coating compositions.

Table 5.3: Thermophysical and physicochemical properties of coatings

Coating	Enthalpy (ΔH) (J/g)	Change in Weight (% ΔW) (g)	Density (ρ) (g/cm ³)	Conductivity (K) (W/mK)	Diffusivity (D) (mm ² /s)	Specific Heat (C) (MJ/m ³ K)
1	-18483.128	14.661	1.471	0.3209	0.264	1.214
2	-11770.027	15.212	1.427	0.3341	0.332	1.004
3	-26157.325	16.151	1.402	0.3026	0.269	1.121
4	-18777.930	17.415	1.467	0.3105	0.375	0.8267
5	-19424.389	15.601	1.488	0.3118	0.311	1.002
6	-22848.611	12.949	1.478	0.2682	0.252	1.062
7	-19845.253	12.544	1.432	0.309	0.3232	0.9572
8	-24956.267	18.464	1.402	0.266	0.2720	0.9781
9	-14819.162	17.405	1.408	0.267	0.2604	1.028
10	-21460.101	18.391	1.390	0.248	0.3011	0.8264
11	-18593.418	14.561	1.400	0.278	0.2816	0.9883
12	-20711.569	15.432	1.420	0.249	0.2540	0.9815
13	-22155.136	18.577	1.440	0.244	0.2349	1.042
14	-17315.139	14.848	1.380	0.264	0.2379	1.109
15	-17811.375	17.725	1.430	0.233	0.2175	1.076
16	-13095.341	16.199	1.440	0.258	0.2625	0.9840
17	-12871.595	15.562	1.360	0.245	0.2443	1.006
18	-13693.785	14.223	1.390	0.267	0.2506	1.069
19	-13482.527	13.161	1.360	0.236	0.2216	1.065
20	-17127.456	14.562	1.390	0.270	0.2314	1.167
21	-17672.234	15.321	1.420	0.271	0.2618	1.038

Table 5.4: Wettability properties of coatings

Coating	Contact Angle (θ) (°)	Surface Tension (γ) (mN/m)	Adhesion Energy (E) (J/m ²)	Spread Area (A) (m ²)
1	58.23	466.63	0.71	6767.87
2	85.34	485.91	0.52	4659.03
3	88.48	479.85	0.49	2660.82
4	74.36	482.59	0.61	2943.57
5	29.04	479.79	0.89	7816.02
6	18.12	452.89	0.90	17898.10
7	82.44	481.00	0.54	3974.98
8	52.55	493.64	0.79	2737.62
9	59.39	489.15	0.73	3312.64
10	20.38	489.05	0.94	11930.20
11	53.93	486.86	0.77	4179.90
12	12.15	475.91	0.95	10033.20
13	14.56	475.18	0.95	14735.30
14	55.58	474.59	0.74	25060.60
15	87.31	495.31	0.51	1493.11
16	16.38	491.99	0.52	2069.34
17	81.17	485.70	0.56	1211.34
18	48.14	472.80	0.78	1616.34
19	85.93	492.23	0.52	1277.56
20	60.42	464.43	0.69	2293.72
21	23.91	484.46	0.76	1613.15

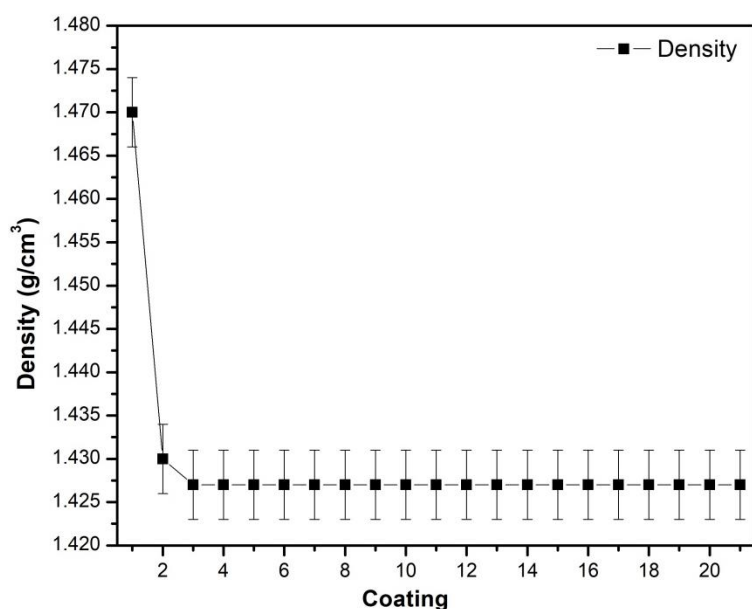


Figure 5.2: Density of coating compositions

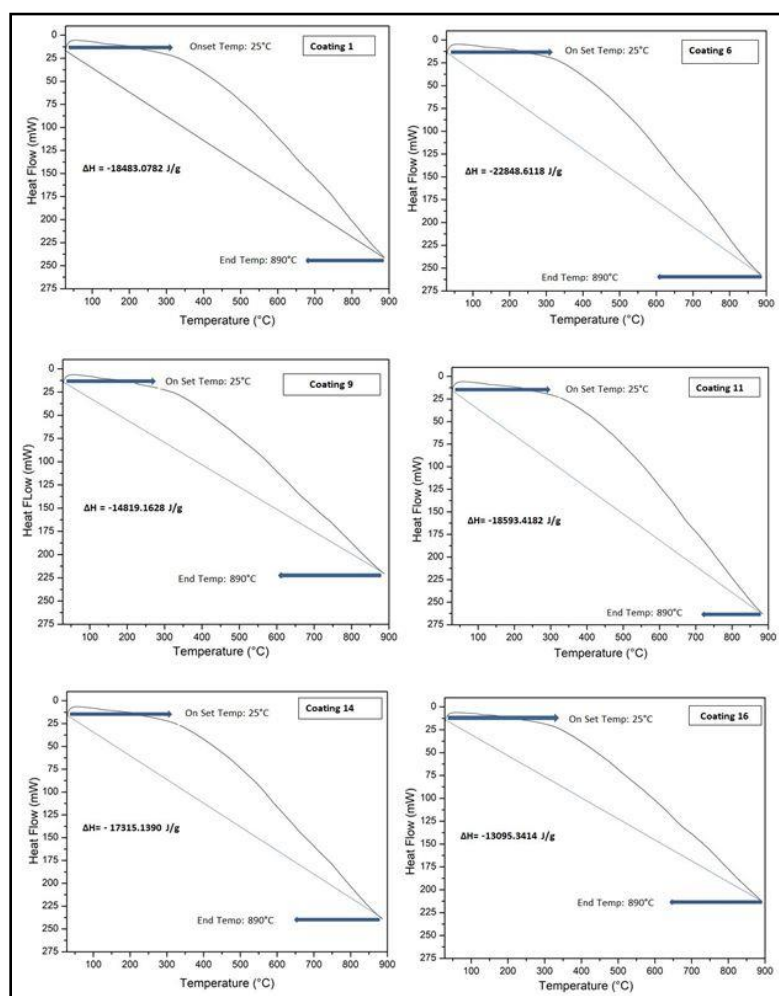


Figure 5.3: Heat flow curve for enthalpy calculation

Figure 5.4 represents the images of partially melt coating pellets, which were then analyzed using Image J software to calculate the wettability parameters.



Figure 5.4: Types of melting and spreading patterns: (a) Complete melting (b) Partial Melting

5.1.3. REGRESSION MODELS FOR ELECTRODE COATING PROPERTIES

The coating properties are majorly dependent on its composition in terms of constituent minerals. Regression models for each of the investigated property were developed to find the influence of constituents and their interactions on the coating properties (equations A1-A10). The developed regression models were analyzed using ANOVA, for their adequacy against the 95% confidence limit ($p < 0.05$). The ANOVA along with model equations were used to establish the synergistic and anti-synergistic effect of coating constituents and their interactions on the properties. ANOVA table for coating properties is given in Table 5.5-5.6.

Table 5.5: ANOVA for physicochemical and thermophysical properties

Response	Source	Sum of Squares	df	Mean Square	F Value	P Value	Significance	R ²
Density	Model	0.010	13	7.85×10^{-4}	4.73	0.0221	Significant	0.74
	Linear Mixture	4.54×10^{-3}	3	1.51×10^{-3}	3.54	0.0375		
	CaO. CaF ₂	1.63×10^{-3}	1	1.63×10^{-3}	0.70	0.4302		
	CaO.TiO ₂	3.00×10^{-4}	1	3.00×10^{-4}	0.13	0.7304		
	CaO.SiO ₂	5.91×10^{-4}	1	5.91×10^{-4}	5.13	0.0176		
	CaF ₂ .TiO ₂	5.45×10^{-5}	1	5.45×10^{-5}	0.023	0.8828		
	CaF ₂ .SiO ₂	1.74×10^{-4}	1	1.74×10^{-4}	0.075	0.7923		
	TiO ₂ .SiO ₂	6.40×10^{-7}	1	6.40×10^{-7}	4.26	0.0293		
	CaO.CaF ₂ .TiO ₂	1.84×10^{-4}	1	1.84×10^{-4}	0.079	0.7868		
	CaO.CaF ₂ .SiO ₂	1.87×10^{-3}	1	1.87×10^{-3}	0.80	0.3999		
	CaO.TiO ₂ .SiO ₂	7.83×10^{-6}	1	7.83×10^{-6}	3.3×10^{-3}	0.9554		
	CaF ₂ .TiO ₂ .SiO ₂	1.73×10^{-3}	1	1.73×10^{-3}	0.74	0.4168		
	Residual	0.016	7	2.33×10^{-3}				
Weight Loss	Model	30.43	13	2.34	7.32	0.0154	Significant	0.77
	Linear Mixture	15.35	3	5.12	1.05	0.4284		
	CaO. CaF ₂	0.014	1	0.014	2.9×10^{-3}	0.9581		
	CaO.TiO ₂	0.24	1	0.24	6.08	0.0251		
	CaO.SiO ₂	1.60	1	1.60	5.27	0.0337		
	CaF ₂ .TiO ₂	0.057	1	0.057	0.012	0.9169		
	CaF ₂ .SiO ₂	2.06	1	2.06	0.42	0.5366		
	TiO ₂ .SiO ₂	0.95	1	0.95	4.65	0.0412		
	CaO.CaF ₂ .TiO ₂	2.88	1	2.88	0.59	0.4675		
	CaO.CaF ₂ .SiO ₂	4.04	1	4.04	0.83	0.3928		
	CaO.TiO ₂ .SiO ₂	0.94	1	0.94	6.38	0.0225		
	CaF ₂ .TiO ₂ .SiO ₂	5.75	1	5.75	1.18	0.3132		
	Residual	34.12	7	4.87				

Enthalpy	Model	2.79x10 ⁸	13	2.62x10 ⁷	7.47	0.0064	Significant	0.93
	Linear Mixture	2.62x10 ⁷	3	8.73x10 ⁶	3.03	0.1026		
	CaO. CaF ₂	8.79x10 ⁶	1	8.79x10 ⁶	3.05	0.1241		
	CaO.TiO ₂	2.16x10 ⁷	1	2.16x10 ⁷	7.52	0.0289		
	CaO.SiO ₂	1.17x10 ⁵	1	1.17x10 ⁵	0.041	0.8459		
	CaF ₂ .TiO ₂	3.83x10 ⁷	1	3.83x10 ⁷	13.31	0.0082		
	CaF ₂ .SiO ₂	253.43	1	253.43	8.79x10 ⁵	0.9928		
	TiO ₂ .SiO ₂	7.99x10 ⁶	1	7.99x10 ⁶	2.78	0.1396		
	CaO.CaF ₂ .TiO ₂	5.22x10 ⁷	1	5.22x10 ⁷	18.13	0.0038		
	CaO.CaF ₂ .SiO ₂	4.59x10 ⁷	1	4.59x10 ⁷	15.97	0.0052		
	CaO.TiO ₂ .SiO ₂	9.37x10 ⁶	1	9.37x10 ⁶	3.25	0.1143		
	CaF ₂ .TiO ₂ .SiO ₂	7.34x10 ⁷	1	7.34x10 ⁷	25.50	0.0015		
	Residual	2.01x10 ⁷	7	2.88x10 ⁶				
	Model	0.011	13	8.22 x 10 ⁻⁴	7.3	0.04716		
Conductivity	Linear Mixture	4.005x10 ⁻³	3	1.33 x 10 ⁻³	1.45	0.3086	Significant	0.82
	CaO. CaF ₂	2.312x10 ⁻⁷	1	2.312x10 ⁻⁷	2.5x10 ⁻⁴	0.9878		
	CaO.TiO ₂	3.291x10 ⁻⁴	1	3.291x10 ⁻⁴	0.36	0.5691		
	CaO.SiO ₂	4.76x10 ⁻⁶	1	4.76 x 10 ⁻⁶	8.1	0.0321		
	CaF ₂ .TiO ₂	1.42x10 ⁻³	1	1.42 x 10 ⁻³	1.55	0.2535		
	CaF ₂ .SiO ₂	8.54x10 ⁻⁶	1	8.54 x 10 ⁻⁶	9.2x10 ⁻³	0.9260		
	TiO ₂ .SiO ₂	1.60x10 ⁻⁶	1	1.60 x 10 ⁻⁶	6.9	0.0387		
	CaO.CaF ₂ .TiO ₂	1.74x10 ⁻³	1	1.74 x 10 ⁻³	1.89	0.2113		
	CaO.CaF ₂ .SiO ₂	1.79x10 ⁻³	1	1.79 x 10 ⁻³	1.94	0.2060		
	CaO.TiO ₂ .SiO ₂	5.42x10 ⁻⁴	1	5.42 x 10 ⁻⁴	8.72	0.02527		
	CaF ₂ .TiO ₂ .SiO ₂	6.86x10 ⁻⁴	1	6.86 x 10 ⁻⁴	0.74	0.4170		
	Residual	6.45x10 ⁻³	7	9.22 x 10 ⁻⁴				
	Model	0.015	13	1.18 x 10 ⁻³	5.1	0.0418	Significant	0.78
	Linear Mixture	1.25x10 ⁻³	3	4.18 x 10 ⁻⁴	0.18	0.9050		
Diffusivity	CaO. CaF ₂	2.78x10 ⁻⁵	1	2.78 x 10 ⁻⁵	0.012	0.9154		
	CaO.TiO ₂	1.39x10 ⁻⁴	1	1.39 x 10 ⁻⁴	0.061	0.8123		
	CaO.SiO ₂	6.48x10 ⁻⁶	1	6.48 x 10 ⁻⁶	2.8x10 ⁻³	0.9591		
	CaF ₂ .TiO ₂	2.92x10 ⁻³	1	2.92 x 10 ⁻³	1.28	0.2960		
	CaF ₂ .SiO ₂	1.83x10 ⁻⁴	1	1.83 x 10 ⁻⁴	0.080	0.7857		
	TiO ₂ .SiO ₂	2.08x10 ⁻⁵	1	2.08 x 10 ⁻⁵	9.1x10 ⁻³	0.9267		
	CaO.CaF ₂ .TiO ₂	9.57x10 ⁻⁴	1	9.57 x 10 ⁻⁴	0.42	0.5391		
	CaO.CaF ₂ .SiO ₂	2.56x10 ⁻³	1	2.56 x 10 ⁻³	1.12	0.3255		
	CaO.TiO ₂ .SiO ₂	4.01x10 ⁻³	1	4.01 x 10 ⁻³	7.15	0.0227		
	CaF ₂ .TiO ₂ .SiO ₂	5.25x10 ⁻⁵	1	5.25 x 10 ⁻⁵	0.023	0.8840		
	Residual	0.016	11	2.29 x 10 ⁻³				
	Model	0.10	13	7.8 x 10 ⁻³	4.73	0.02913	Significant	0.71
	Linear Mixture	0.044	3	0.015	1.46	0.3065		
Specific Heat	CaO. CaF ₂	6.472x10 ⁻⁴	1	6.47 x 10 ⁻⁴	0.064	0.8072		
	CaO.TiO ₂	0.012	1	0.012	1.15	0.3196		
	CaO.SiO ₂	3.87x10 ⁻⁶	1	3.87 x 10 ⁻⁶	3.84	0.03761		
	CaF ₂ .TiO ₂	3.2x10 ⁻³	1	3.2 x 10 ⁻³	0.32	0.5906		
	CaF ₂ .SiO ₂	1.57x10 ⁻³	1	1.57 x 10 ⁻³	0.16	0.7041		
	TiO ₂ .SiO ₂	2.11x10 ⁻⁴	1	2.11 x 10 ⁻⁴	0.021	0.8889		
	CaO.CaF ₂ .TiO ₂	1.81x10 ⁻³	1	1.81 x 10 ⁻³	0.18	0.6844		
	CaO.CaF ₂ .SiO ₂	2.39x10 ⁻³	1	2.39 x 10 ⁻³	5.79	0.01793		
	CaO.TiO ₂ .SiO ₂	0.014	1	0.014	1.40	0.2753		
	CaF ₂ .TiO ₂ .SiO ₂	4.35x10 ⁻³	1	4.35 x 10 ⁻³	0.43	0.5320		
	Residual	0.071	11	0.010				

Table 5.6: ANOVA for wettability properties

Response	Source	Sum of Squares	df	Mean Square	F Values	P Values	Significance	R ²
Contact Angle	Model	6571.14	9	730.13	7.18	0.03251	Significant	0.86
	Linear Mixture	5275.62	3	1758.54	1.71	0.2229		
	CaO. CaF ₂	146.61	1	146.61	5.76	0.04713		
	CaO.TiO ₂	45.78	1	45.78	0.044	0.8369		
	CaO.SiO ₂	121.71	1	121.71	6.73	0.03896		
	CaF ₂ .TiO ₂	587.77	1	587.77	0.57	0.4658		
	CaF ₂ .SiO ₂	164.62	1	164.62	0.16	0.03969		
	TiO ₂ .SiO ₂	448.42	1	448.42	6.49	0.5229		
	Residual	11327.47	11	1029.77				
Surface Tension	Model	2279.58	9	253.29	13699.56	<0.0001	Significant	0.99
	Linear Mixture	2279.14	3	759.71	41090.87	<0.0001		
	CaO. CaF ₂	0.32	1	0.32	17.31	0.0016		
	CaO.TiO ₂	0.053	1	0.053	2.87	0.1182		
	CaO.SiO ₂	0.053	1	0.053	2.88	0.1177		
	CaF ₂ .TiO ₂	1.782x10 ⁻³	1	1.782x10 ⁻³	0.096	0.7620		
	CaF ₂ .SiO ₂	0.025	1	0.025	1.34	0.2719		
	TiO ₂ .SiO ₂	3.905x10 ⁻³	1	3.905x10 ⁻³	0.21	0.6548		
	Residual	0.20	11	0.018				
Adhesion Energy	Model	0.24	13	0.018	6.851	0.02888	Significant	0.89
	Linear Mixture	0.10	3	0.033	0.85	0.50940		
	CaO. CaF ₂	0.013	1	0.013	6.272	0.03586		
	CaO.TiO ₂	4.15x10 ⁻³	1	4.15x10 ⁻³	0.11	0.75490		
	CaO.SiO ₂	0.049	1	0.049	6.577	0.03030		
	CaF ₂ .TiO ₂	1.941x10 ⁻³	1	1.941x10 ⁻³	0.049	0.83060		
	CaF ₂ .SiO ₂	0.034	1	0.034	6.962	0.02817		
	TiO ₂ .SiO ₂	0.073	1	0.073	1.86	0.2151		
	CaO.CaF ₂ .TiO ₂	0.011	1	0.011	0.28	0.6130		
	CaO.CaF ₂ .SiO ₂	0.010	1	0.010	7.353	0.02629		
	CaO.TiO ₂ .SiO ₂	0.039	1	0.039	1.00	0.3504		
	CaF ₂ .TiO ₂ .SiO ₂	1.805x10 ⁻⁵	1	1.805x10 ⁻⁵	4.58x10 ⁻⁴	0.9835		
	Residual	0.28	7	0.039				
	Residual	0.28	7	0.039				
Spread Area	Model	2.826x10 ⁸	13	2.174x10 ⁷	5.84	0.04834	Significant	0.92
	Linear Mixture	1.324x10 ⁸	3	4.415x10 ⁷	1.84	0.2274		
	CaO. CaF ₂	2.639x10 ⁷	1	2.639x10 ⁷	1.10	0.0328		
	CaO.TiO ₂	2.427x10 ⁶	1	2.427x10 ⁶	7.32	0.3591		
	CaO.SiO ₂	5.99x10 ⁶	1	5.990x10 ⁶	0.25	0.0324		
	CaF ₂ .TiO ₂	9.992x10 ⁶	1	9.992x10 ⁶	0.42	0.0430		
	CaF ₂ .SiO ₂	1.465x10 ⁶	1	1.465x10 ⁶	0.061	0.8118		
	TiO ₂ .SiO ₂	4.199x10 ⁵	1	4.199x10 ⁵	6.72	0.0389		
	CaO.CaF ₂ .TiO ₂	4.832x10 ⁷	1	4.832x10 ⁷	2.02	0.1985		
	CaO.CaF ₂ .SiO ₂	4.367x10 ⁶	1	4.367x10 ⁶	0.18	0.6822		
	CaO.TiO ₂ .SiO ₂	5.916x10 ⁶	1	5.916x10 ⁶	0.25	0.6344		
	CaF ₂ .TiO ₂ .SiO ₂	6.625x10 ⁶	1	6.625x10 ⁶	8.24	0.0261		
	Residual	1.677x10 ⁸	7	2.395x10 ⁷				
	Residual	1.677x10 ⁸	7	2.395x10 ⁷				

ANOVA along with model equations helped us to identify the constituents and interactions which have synergistic and anti-synergistic effects on specific properties (Table 5.7-5.8).

Table 5.7: Effect of coating constituents on physicochemical and thermophysical properties

Interaction	Constituent	Density	Weight	Enthalpy	Conductivity	Diffusivity	Specific Heat
Individual	CaO	-	0	0	0	0	0
	CaF ₂	-	0	0	0	0	0
	TiO ₂	-	0	0	0	0	0
	SiO ₂	+	0	0	0	0	0
Binary	CaO. CaF ₂	0	0	0	0	0	0
	CaO.TiO ₂	0	+	+	0	0	0
	CaO.SiO ₂	+	-	0	+	0	-
	CaF ₂ .TiO ₂	0	0	+	0	0	0
	CaF ₂ .SiO ₂	0	0	+	0	0	0
	TiO ₂ .SiO ₂	-	-	0	+	0	0
Tertiary	CaO.CaF ₂ .TiO ₂	0	0	-	0	0	0
	CaO.CaF ₂ .SiO ₂	0	0	0	0	0	+
	CaO.TiO ₂ .SiO ₂	0	+	0	-	+	0
	CaF ₂ .TiO ₂ .SiO ₂	0	0	-	0	0	0

[+: Synergistic, - : Anti Synergistic, 0: No effect]

Table 5.8: Effect of coating constituents on wettability properties

Nature	Term	Contact Angle	Surface Tension	Adhesion Energy	Spread Area
Individual	CaO	0	+	0	0
	CaF ₂	0	+	0	0
	TiO ₂	0	+	0	0
	SiO ₂	0	+	0	0
Binary	CaO. CaF ₂	-	+	+	+
	CaO.TiO ₂	0	0	0	0
	CaO.SiO ₂	+	0	-	-
	CaF ₂ .TiO ₂	-	0	0	+
	CaF ₂ .SiO ₂	-	0	-	+
	TiO ₂ .SiO ₂	-	0	0	-
Tertiary	CaO.CaF ₂ .TiO ₂	0	0	0	0
	CaO.CaF ₂ .SiO ₂	0	0	+	0
	CaO.TiO ₂ .SiO ₂	0	0	0	0
	CaF ₂ .TiO ₂ .SiO ₂	0	0	0	+

[+: Synergistic, - : Anti Synergistic, 0: No effect]

Analysis of the regression model indicates that coating constituents affect the thermal and physicochemical properties of electrode coating significantly. The electrode coating is subjected to high-temperature ranges during the welding process. Exposure to high temperature causes several chemical reactions to occur. Sound performance in such an environment requires high thermal stability, minimum weight loss, and suitable enthalpy of the fusion reaction, increased thermal conductivity, suitable diffusivity, and specific heat. Individual behavior of coating mineral constituents, along with their interaction with each other determines their performance characteristic. Coating mixture melts and gets dissolved into the molten weld pool with base metal and filler wire. The density of the coating mixture should be good to ensure restricted fluidity of the weld pool. A highly fluid weld pool will lead to spreading before solidification and can give rise to several defects. SiO₂ is known as network/chain former, which decreases fluidity and increases the density of the pool. CaO and SiO₂ together form SiO₄⁴⁻ complex ion by the following chemical reaction: $\text{CaO} = \text{Ca}^{2+} + \text{O}^{2-}$; $\text{SiO}_2 + 2\text{O}^{2-} = \text{SiO}_4^{4-}$. This complex ion makes the diffusion of inclusions difficult and hence increases density. As per regression model

individual constituents SiO_2 and its binary interaction with CaO has a synergistic effect on the density of the coating. The developed cubic regression model has a p-value of 0.0221 which is under the acceptable confidence level of 95%. The coating is expected to be thermally stable at high temperatures. Thermal stability in this work has been measured using thermo gravimetric analyzer where weight loss has been calculated by heating in a controlled environment. As per the regression model analysis for weight loss, it is clearly evident that binary interactions CaO.TiO_2 and tertiary interaction $\text{CaO.TiO}_2.\text{SiO}_2$ tend to increase the thermal stability of coating. This model stands significant with p-value of 0.0154. Enthalpy is defined as the amount of energy in the form of heat, released or absorbed during chemical reactions. In this experiment, all enthalpy values came out to be negative, suggesting the reaction to be exothermic in nature. The enthalpy value should neither be too high nor too low. A very high negative value of enthalpy will mean, during the welding process the amount of heat released will be very high. This is not desirable as high heat produced will affect the base metal and will lead to increased heat affected zone area and other related issues. The regression model of enthalpy is significant with p value of 0.0064. Binary interactions CaO.TiO_2 , $\text{CaF}_2.\text{TiO}_2$, $\text{CaF}_2.\text{SiO}_2$ are synergistic to enthalpy. Synergistic interactions indicate that CaF_2 and TiO_2 are quite instrumental in increasing enthalpy value. Thermal properties of conductivity, diffusivity and specific heat are also significantly dependent on coating composition. Regression model shows dependency of thermal conductivity on synergistic binary interactions of CaO.SiO_2 , $\text{TiO}_2.\text{SiO}_2$ with p value of model being 0.0064. Similarly thermal diffusivity has a significant regression model with p value 0.0418 and its synergistic factor is tertiary interaction of calcite, rutile and silica. Specific heat is the amount of heat required to produce unit increase in temperature of unit mass of coating mixture. Specific heat should not be very high as it will require lots of energy to provide melting and fusion heat to electrode. On the other hand low specific heat will cause the temperature to increase from a very low heat input and will correspondingly cause very high temperature during the process. This will eventually lead to release of a huge amount of heat in an exothermic process and will affect the weld adversely. As per regression model with p value of 0.02913, the synergistic factors for specific heat is tertiary interaction $\text{CaO.CaF}_2.\text{SiO}_2$. For the wettability properties, analysis of the regression model indicates that individual coating constituent minerals and their binary, tertiary interactions affect wettability properties significantly. Chemical reactions and subsequent structural changes influence the molten coating's characteristics. Available free oxygen plays an important role in contact angle modification. Strong basic oxides CaO undergoes reduction reaction $[\text{CaO} = \text{Ca}^{2+} + 2\text{O}^-]$ and provides sufficient free oxygen. As per the network modification theory, the free fluoride ion from CaF_2 breaks the bridging bonds of the Si-O slag network. This leads to the depolymerization of complex silicate $[\text{SiO}_4^{4-}]$ ion [Kim et al., 2011, Kim et al., 2016]. The regression model suggests the binary interaction CaO.CaF_2 , CaO.SiO_2 and $\text{CaF}_2.\text{SiO}_2$ have a synergistic effect on contact angle property. The quadratic regression model of surface tension lies well under the acceptance confidence limit [p value] of 95 %. The individual constituents and the binary interaction of CaO.CaF_2 have a synergistic effect on surface tension property. Adhesion work is the energy required per unit area to remove contacting material at the interface of liquid and substrate. Adhesion in behavior is absolutely opposite to contact angle. As the contact angle decreases, better is the flow of molten slag, and adhesion energy increases. Special cubic regression model for adhesion with confidence value lying under 95% suggests tertiary interaction of $\text{CaO.CaF}_2.\text{SiO}_2$ to have a synergistic effect on it. Spreading area is inversely proportional to the contact angle. As the contact angle decrease, the height of the slag layer decreases, and hence the spread ability of the molten pool of coating increases. The interactions having a synergistic effect on contact angle have an opposite effect on the spreading area. Based on the actual and predicted values obtained from experiment and regression equations, a plot between act the two was obtained for each of the properties. The plot indicates the closeness of the experimental values to the line of best fit as obtained from the regression models. The predicted versus actual plots for the electrode coating properties is presented in Figure 5.5 and 5.6 for the physicochemical-thermophysical and wettability properties respectively.

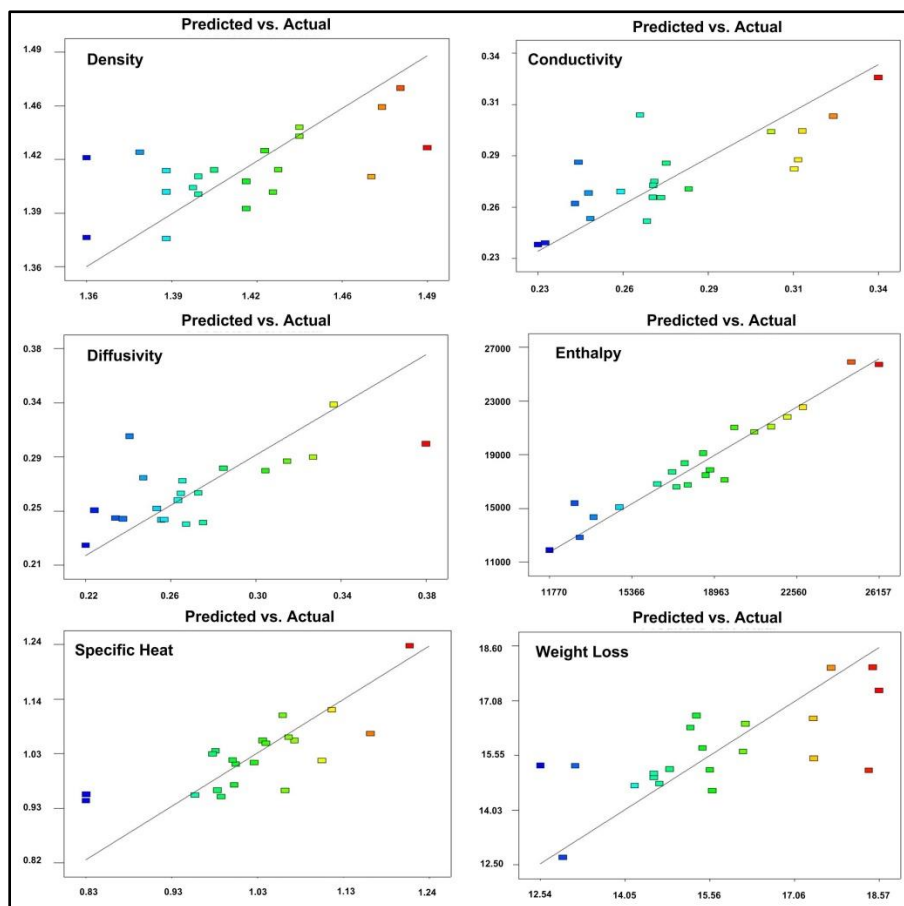


Figure 5.5: Predicted versus Actual plots for physicochemical-thermophysical properties

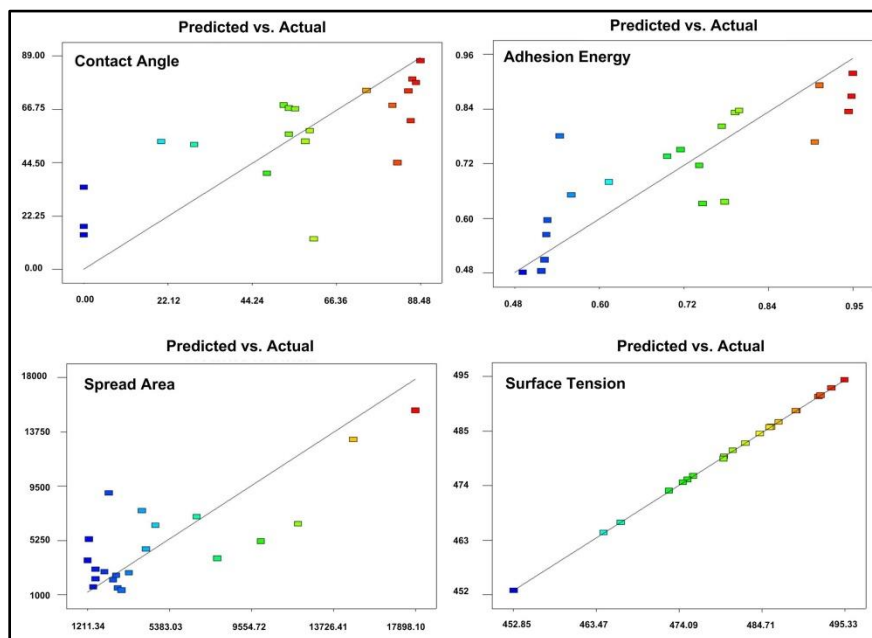


Figure 5.6: Predicted versus Actual plots for wettability properties

To have a better understanding of the variation in the response values of different properties with varying constituent compositions, contour graph for each of the property was plotted. Contour plots are the representation of variation of response value over the changing value of input parameters. The different colors of contour show the different range of values of a particular response. Moreover the lines running across the plot represent the constant value of

output response with the variation in mixture composition. Figure 5.7 and 5.8 represents contour plot for the measured physicochemical-thermo physical and wettability properties.

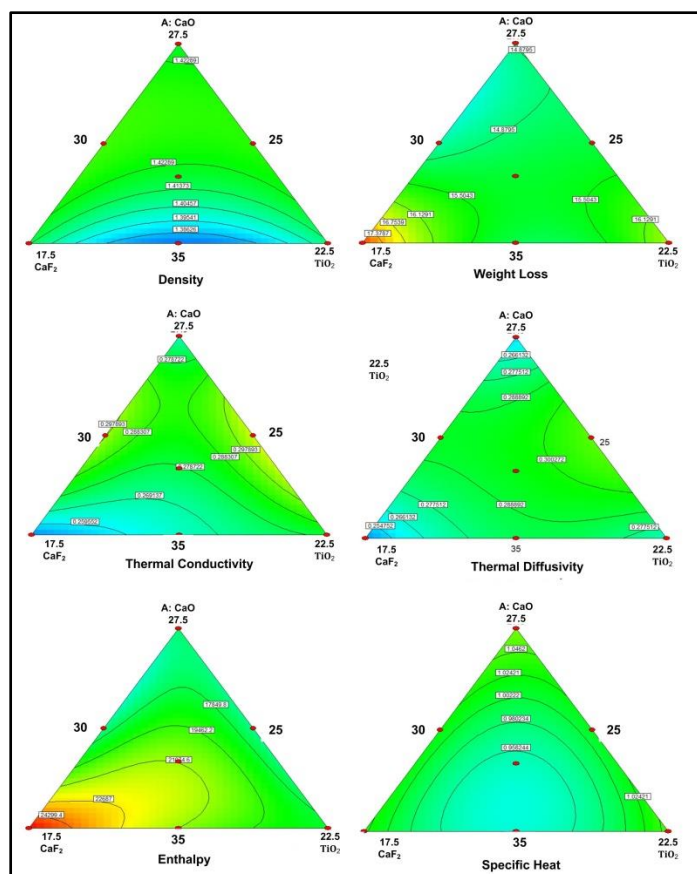


Figure 5.7: Contour plots for physicochemical-thermophysical properties

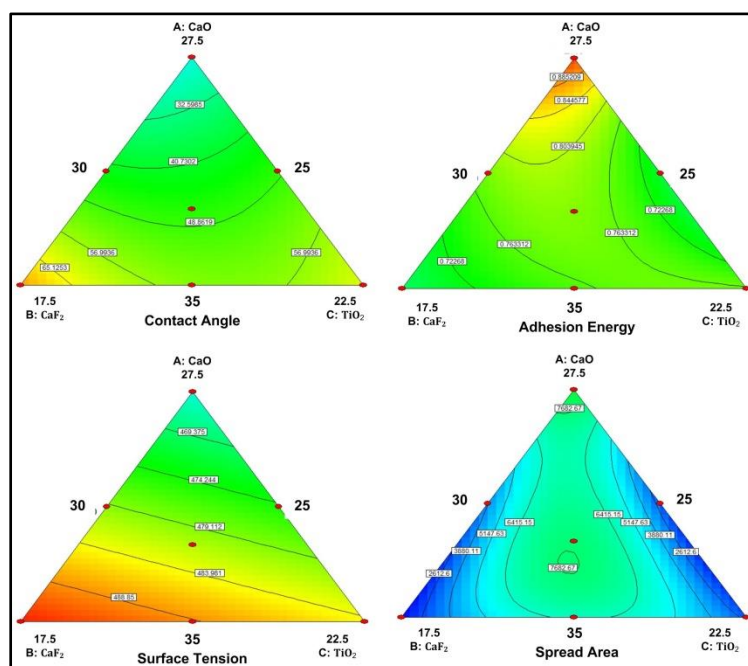


Figure 5.8: Contour plots for wettability properties

The developed regression models were further validated by calculating the error percentage between the experimental and model values for all properties, three electrode coating compositions chosen at random from the design matrix. The experimental results and model values were obtained for each of these compositions characterized for different properties. The

results of the same is represented in Table 5.9 which shows that %error for all the properties lies below or around 5%, which is in the acceptable limit, validating the model.

Table 5.9: Model validation for electrode coating properties

				Predicted value			Actual Value			%Error		
CaO	CaF ₂	TiO ₂	SiO ₂	ρ	ΔW	TC	ρ	ΔW	TC	ρ	ΔW	TC
30	24.5	25.5	10	1.44	14.75	0.25	1.47	14.63	0.24	2.11	0.85	4.16
34	21	29	6	1.41	17.92	0.26	1.49	17.54	0.24	5.61	2.14	7.65
31	20	29.5	9.5	1.39	14.69	0.28	1.31	14.18	0.27	5.72	3.43	3.57
CaO	CaF ₂	TiO ₂	SiO ₂	ΔH	ΔW	TD	ΔH	ΔW	TD	ΔH	ΔW	TD
30	24.5	25.5	10	19097.8	14.76	0.24	18483.1	14.16	0.25	3.2	4.1	4.2
34	21	29	6	16736.5	17.97	0.25	17811.1	17.22	0.24	6.4	4.2	4.1
31	20	29.5	9.5	14329.8	14.69	0.22	13693.7	14.22	0.23	4.4	3.2	4.5
CaO	CaF ₂	TiO ₂	SiO ₂	SH	CA	AE	SH	CA	AE	SH	CA	AE
30	24.5	25.5	10	1.27	53.83	0.79	1.21	56.8	0.75	4.7	5.5	5.1
34	21	29	6	1.02	44.68	0.59	1.07	47.3	0.55	4.9	5.7	6.7
31	20	29.5	9.5	1.09	43.53	0.83	1.06	46.1	0.78	2.7	5.9	4.8
CaO	CaF ₂	TiO ₂	SiO ₂	ST	SA		ST	SA		ST	SA	
30	24.5	25.5	10	462.5	7115.2		456.63	6867.57		1.3	3.4	
34	21	29	6	497.7	1597.0		489.81	1710.21		1.6	7.1	
31	20	29.5	9.5	470.9	1978.9		462.81	2035.97		1.9	2.8	

[ρ : Density, ΔW : % loss in weight, ΔH : Enthalpy of fusion, K: Thermal conductivity, D: Thermal diffusivity, S: Specific heat, CA: Contact angle, E: Adhesion energy, ST: Surface tension, SA: Spread area]

5.1.4. STRUCTURAL CHARACTERIZATION OF ELECTRODE COATINGS

Structural characterization of coating mixtures was done using X-Ray Diffraction (XRD) and Fourier Transformation Infrared Spectroscopy (FTIR) (Figure 5.9). XRD of all the coating mixtures is almost the same because of same constituent mixture present in them. CaCO₃ in the form of veterite, SiO₂ in the form of silica and quartz, CaTiSiO₃, TiO₂, CaO and CaF correspond to the major peaks of XRD spectra.

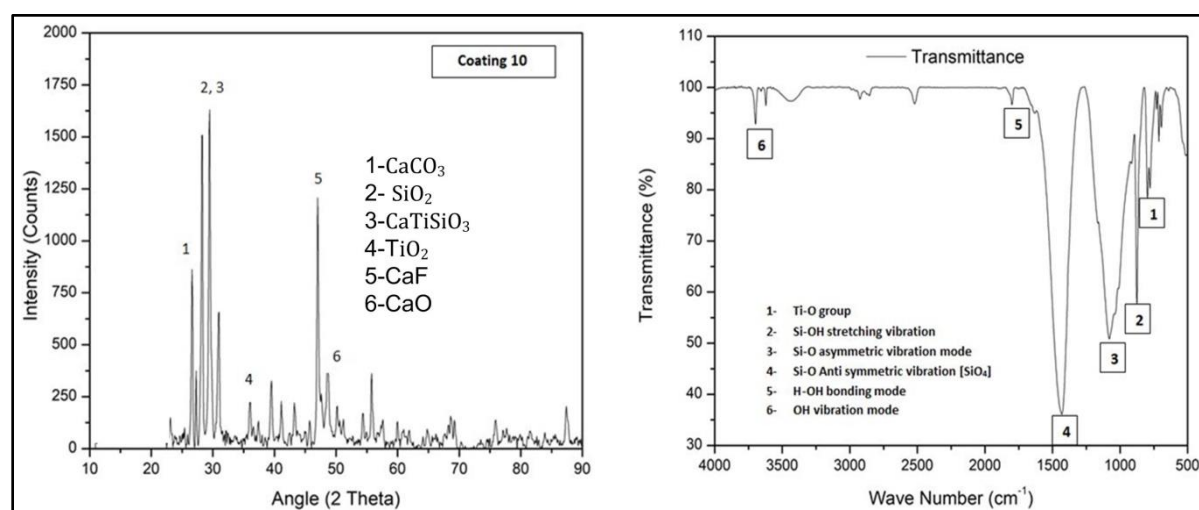


Figure 5.9: XRD and FTIR plots of electrode coating

FTIR curve between transmittance and wave number is also almost similar for all coating specimens. This is because constituent components in all coatings are the same. The difference in composition leads to variation in peak intensities. Distinguished peaks are observed in different regions across the entire wavenumber span. A peak in the region of 700-750 cm⁻¹ corresponds to symmetric stretching of Titanyl group (Ti-O), whereas the one lying in the region

750-800 cm^{-1} represents Si-OH stretching vibrations occurring in the mixture. Peak in 1000-1250 cm^{-1} corresponds to Si-O asymmetric vibration mode. Asymmetric vibration of Si-O due to the formation of complex SiO_4^{4-} ion is shown by peak lying in 1250-1500 cm^{-1} area. Small peaks in the region of 1500-1750 cm^{-1} and 3250-3500 cm^{-1} along with adjoining areas represent H-OH bonding and OH vibration mode respectively.

5.1.5. UTILIZATION OF MINERAL WASTE RED OCHRE AS ELECTRODE COATING CONSTITUENT

In the present era of rapid industrialization and development, the utilization of mineral waste in 'as-is' state is comparatively way too under-explored as compared to its actual potential. Red ochre being a waste from iron ore can be bought into use, where its high iron concentration can be well utilized. In welding consumable development, it can also be used as a replacement for commercial ferro-alloy powder. This section characterizes the red ochre for various thermophysical, physicochemical, surface, and structural properties to ascertain its suitability for application in SMAW electrode coating composition along with other secondary engineering applications. The thermal properties of red ochre were estimated using hot disc apparatus, which calculated its thermal conductivity to be 0.29 W/mK, thermal diffusivity as 0.213 mm^2/s , whereas the specific heat was found to be 1.39 $\text{MJ}/\text{m}^3\text{K}$ (Figure 5.10). Similarly the weight loss as a measure of thermal stability and enthalpy of fusion upon exposure to 900°C temperature in a controlled environment was found to be 2.21% and -15454.07 J/g (Figure 5.11). The BET surface area analysis determined the specific surface area of red ochre to be 0.644 g/m^2 and the average pore radius to be 41.87 Å. The BET plot for red ochre is represented in Figure 5.12. The thermal properties were found to be in acceptable range as compared to in range with that of the SMAW electrode coatings.

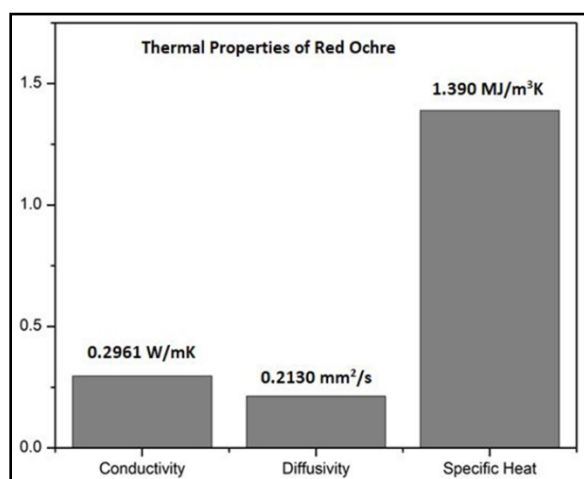


Figure 5.10: Thermal properties of red ochre

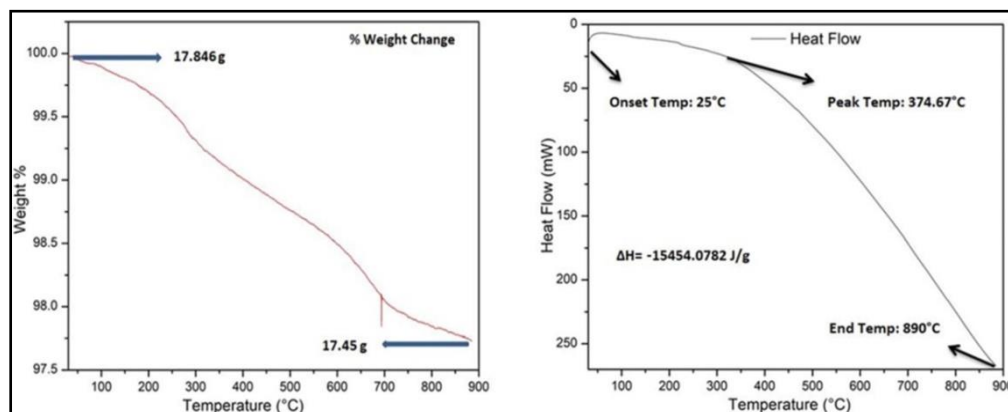


Figure 5.11: Weight loss and enthalpy of red ochre

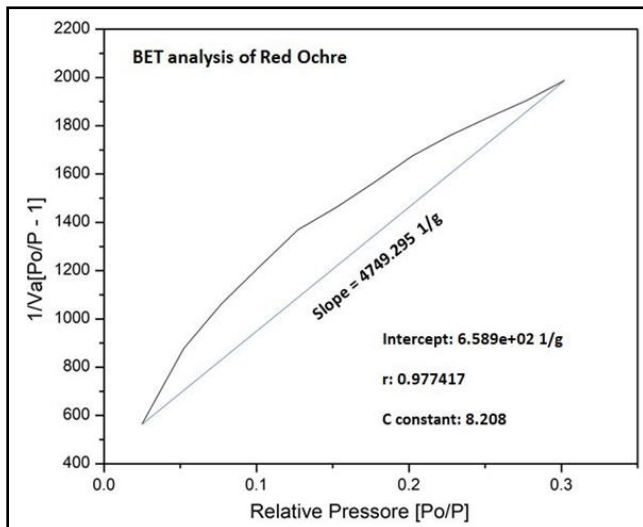


Figure 5.12: BET surface analysis plot of red ochre

Structural characterization of red ochre was done using X-Ray Diffraction XRD and Fourier Transformation Infrared Spectroscopy FTIR (Figure 5.13). XRD analysis shows the presence of iron (III) oxide in the form of haematite, which is the principal ore and as burnt ochre. Silica is also a major constituent in the form of quartz. A complex oxide of iron and silica, namely nontronite, is also present in the ochre powder. FTIR analysis of red ochre shows the presence of various bonds and bond lengths. Peaks in the region of 500-750 cm^{-1} and 2750-3000 cm^{-1} wave number represent Al-O-Al, Al-O and Fe-O bond owing to the presence of Al_2O_3 and Fe_2O_3 respectively. Silica gets oxidized by bacteria from slime, resulting in the formation of SiO_2 and silicate $[\text{SiO}_4^{4-}]$ ion. Asymmetric and anti-symmetric Si-O vibrational bond is present in the compound and is represented by the peaks falling in 1000-1500 cm^{-1} range. Red ochre picks up a considerable amount of moisture owing to its exposure to open environment and drain of mineral tailings, which is majorly in the liquid state. H-OH and OH vibrations bonds are present in the region of 1500-1750 cm^{-1} and 3500-3750 cm^{-1} .

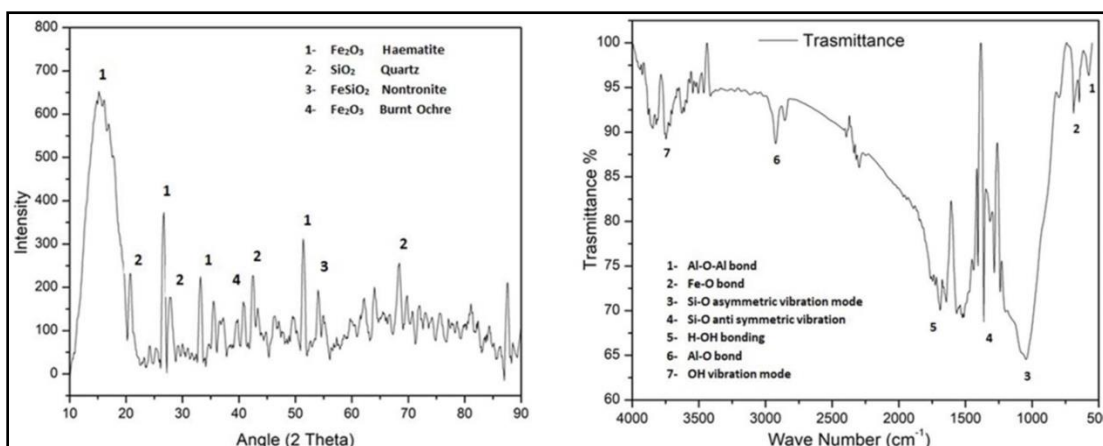


Figure 5.13: Structural characterization of red ochre

5.2. DEVELOPMENT OF SMAW ELECTRODE AND MULTI PASS BEAD ON PLATE EXPERIMENTATION

The coatings formulated, prepared, and characterized in section 5.1 were then extruded on the core filler wire austenitic stainless steel 309L grade. The extrusion process was performed on a laboratory scale electrode extruder. The twenty set of extruded electrodes were air dried

overnight and then baked in an electric oven for 90 minutes at a temperature of 360°C. The extruded electrodes were then used to apply multi pass beads on plate on super duplex stainless steel substrate for each of the coating composition. The schematic of the results discussed in this section is given in Figure 5.14.

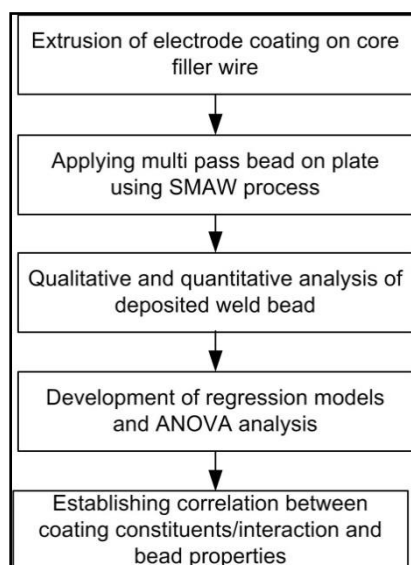


Figure 5.14: Schematic of multi pass bead on plate experiment

5.2.1. QUALITATIVE EXAMINATION OF MULTI PASS BEAD ON PLATE

The applied six multi pass weld beads for each coating composition made electrode were visually examined for qualitative properties in-situ and post bead applying. The in situ observations included the smoke produced, ease of arc ignition, and arc continuity. The post bead laying observations included slag detachability, measured using three-tap test to compare the bead appearance. Figure 5.15 represents multi pass weld bead made using electrodes developed in this study.

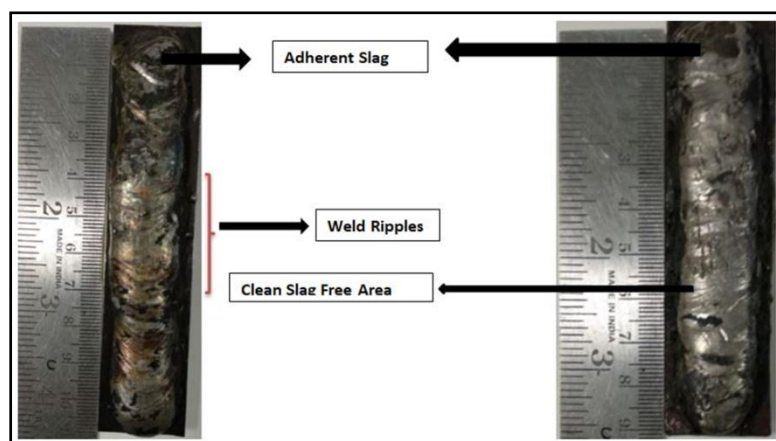
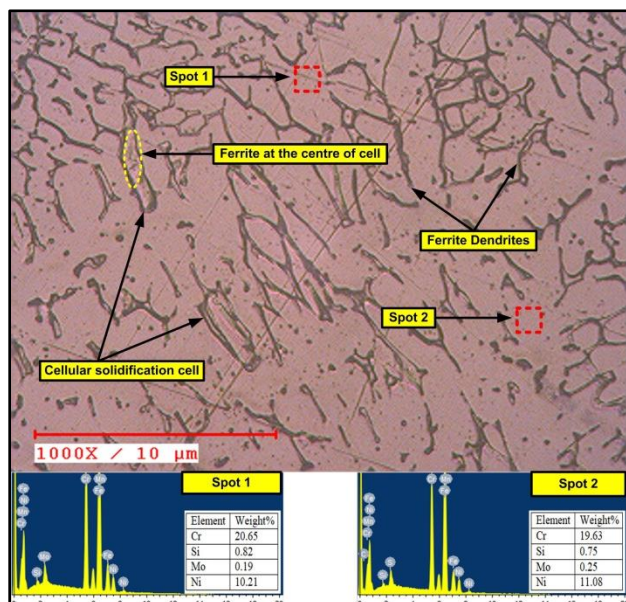


Figure 5.15: Multi pass bead made using laboratory developed electrodes

5.2.2. BEAD MICROSTRUCTURE AND DILUTION

The beads were polished on emery papers from grit size 80-2000, followed by 0.5µm alumina suspension. The polished specimens were electrochemically etched with 10% oxalic acid solution before examining for microstructure on scanning electron microscope (SEM). The microstructure of the multi-pass bead on the plate comprises of primary δ -ferrite and austenite (γ). δ -ferrite lies at the center region of solidification cells. The solidification cells are surrounded by austenite (γ). Ferrites appear in a lacy morphology. The cellular austenite solidifies at the interdendritic region of the dendritic ferrites. The peak tip of the austenite phase

has a curvature pointed towards the solid-liquid interface. The formation of austenite and ferrite progresses as per the eutectic reaction. Due to the welding speed, the formation of ferrite dendrites is favored over eutectic products as the molten metal gets pushed out of the coupled zone. Hence the cellular austenite appears distinctively in the microstructure and is often referred to as the divorced eutectic product. The formation of this microstructure is a resultant product of eutectic/peritectic reaction occurring in the weld fusion zone during solidification and cyclic heating-cooling occurring due to multi-pass welding. Core filler wire being the same, the solidification and corresponding microstructure was found to be the same for all the beads, although no unwanted precipitation was observed in any of them. Figure 5.16 below represents microstructure of bead applied using laboratory developed electrodes along with elemental composition using EDS.



5.16: Microstructure of multi pass beads applied using laboratory developed Electrode 21

The bead was cut across the cross-section and image was captured using a stereomicroscope. This image was further analyzed using Image J software to find the weld penetration and dilution. The dilution majorly depends upon the heat input, which has been the same for all the beads, hence only a small deviation in bead dilution has been observed. Figure 5.17 represents the dilution for some of the beads.

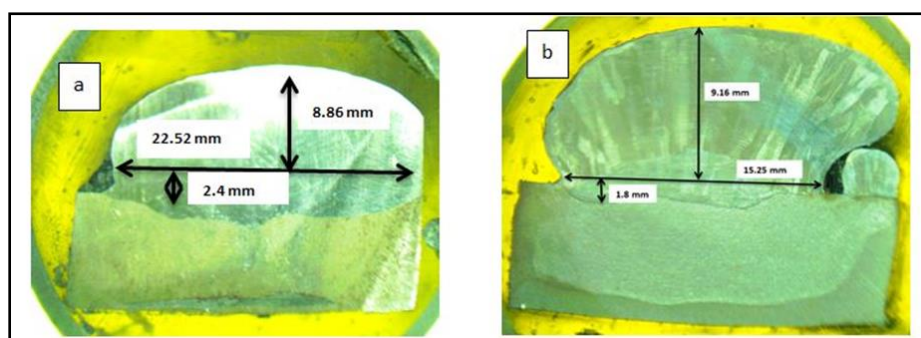


Figure 5.17: Dilution for multi pass beads on plate applied using laboratory developed: (a) Electrode 3 (b) Electrode 21

5.2.3. MICROHARDNESS MEASUREMENT OF MULTI PASS BEAD ON PLATE

The microhardness was measured using Vickers microhardness tester with diamond indenter. The micro hardness measurement plot for twenty one beads carried out using 0.5 kgf load with

a dwell time of 10 seconds is shown in Figure 5.18 Three measurement of hardness was made for each bead, and the average microhardness has been reported here.

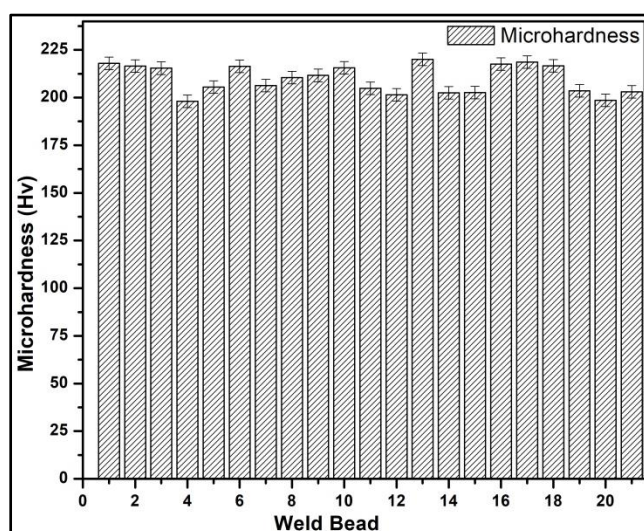


Figure 5.18: Microhardness plot for multi-pass weld beads

5.2.4. MULTI PASS BEAD ON PLATE WELD CHEMISTRY

The weld metal chemistry for twenty one beads on plate obtained using atomic absorption spectrometer is summarized in Table 5.10. Three measurements were made for each bead and average value has been reported here for the comparison and analysis purpose.

Table 5.10: Chemical Composition of Beads (% wt.)

Bead	Carbon	Silicon	Manganese	Chromium	Nickel	Phosphorous	Sulphur	Molybdenum
1	0.028	0.252	0.426	17.802	12.886	0.035	0.012	0.078
2	0.027	0.238	0.553	16.860	12.031	0.028	0.015	0.079
3	0.026	0.223	0.592	18.673	12.077	0.028	0.018	0.096
4	0.028	0.188	0.466	17.899	12.731	0.301	0.017	0.076
5	0.026	0.206	0.431	16.550	12.382	0.030	0.019	0.081
6	0.027	0.235	0.340	16.678	12.864	0.029	0.018	0.058
7	0.028	0.209	0.531	17.588	12.464	0.028	0.017	0.089
8	0.027	0.219	0.704	19.537	11.776	0.027	0.020	0.100
9	0.030	0.218	0.522	19.730	12.568	0.031	0.018	0.107
10	0.032	0.233	0.627	19.789	12.532	0.033	0.017	0.121
11	0.029	0.206	0.718	20.054	12.613	0.032	0.021	0.106
12	0.025	0.194	0.669	19.630	12.259	0.029	0.019	0.114
13	0.022	0.270	0.720	19.701	12.473	0.028	0.012	0.116
14	0.023	0.200	0.615	19.599	12.299	0.031	0.017	0.108
15	0.028	0.201	0.575	19.126	12.522	0.028	0.018	0.107
16	0.029	0.243	0.574	19.050	12.288	0.028	0.020	0.107
17	0.026	0.275	0.788	20.213	12.564	0.030	0.020	0.121
18	0.025	0.263	0.754	19.866	12.535	0.026	0.020	0.117
19	0.028	0.201	0.741	20.248	12.364	0.028	0.018	0.122
20	0.028	0.185	0.617	19.870	12.551	0.033	0.021	0.101
21	0.027	0.205	0.566	19.234	12.381	0.035	0.018	0.110

5.2.5. REGRESSION MODELS FOR MULTI PASS BEAD ON PLATE: WELD METAL CHEMISTRY AND MICROHARDNESS

The weld bead properties are dependent on electrode coating composition. Regression models for microhardness and elements in weld chemistry were developed to establish the influence of constituents and their interactions (A11-A19). The developed regression models were subjected

to ANOVA test, for their adequacy against the 95% confidence limit ($p < 0.05$) and establishing the synergistic and anti-synergistic effect of electrode coating constituents/interactions. ANOVA table for multi pass bead chemistry and microhardness is given in Table 5.11.

Table 5.11: ANOVA for multi pass bead on plate weld chemistry and properties

Response	Source	Sum of Squares	df	Mean Square	F Values	P Values	Significance	R ²
Carbon	Model	6.931×10^{-5}	13	5.332×10^{-6}	4.31	0.0451	Significant	0.81
	Linear Mixture	1.584×10^{-5}	3	5.280×10^{-6}	1.20	0.3760		
	CaO. CaF ₂	1.021×10^{-5}	1	1.021×10^{-5}	5.21	0.0278		
	CaO.TiO ₂	9.573×10^{-10}	1	9.537×10^{-10}	4.87	0.0355		
	CaO.SiO ₂	1.093×10^{-6}	1	1.093×10^{-6}	0.25	0.6329		
	CaF ₂ .TiO ₂	3.603×10^{-7}	1	3.603×10^{-7}	6.73	0.0192		
	CaF ₂ .SiO ₂	1.391×10^{-6}	1	1.391×10^{-6}	0.32	0.5907		
	TiO ₂ .SiO ₂	5.97×10^{-7}	1	5.97×10^{-7}	0.14	0.7230		
	CaO.CaF ₂ .TiO ₂	6.395×10^{-6}	1	6.935×10^{-6}	4.55	0.0421		
	CaO.CaF ₂ .SiO ₂	3.086×10^{-6}	1	3.086×10^{-6}	0.70	0.4291		
	CaO.TiO ₂ .SiO ₂	2.301×10^{-6}	1	2.301×10^{-6}	0.53	0.4922		
	CaF ₂ .TiO ₂ .SiO ₂	1.033×10^{-5}	1	1.033×10^{-5}	2.36	0.1687		
	Residual	3.068×10^{-5}	7	4.83×10^{-6}				
Nickel	Model	0.51	3	0.17	3.25	0.0477	Significant	0.77
	Linear Mixture	0.51	3	0.17	3.25	0.0477		
	Residual	0.88	17	0.52				
Chromium	Model	16.68	13	1.28	4.73	0.0477	Significant	0.87
	Linear Mixture	5.84	3	1.95	1.10	0.4097		
	CaO. CaF ₂	1.69	1	1.69	6.54	0.0218		
	CaO.TiO ₂	0.11	1	0.11	6.51	0.0228		
	CaO.SiO ₂	0.68	1	0.68	0.39	0.5539		
	CaF ₂ .TiO ₂	2.53	1	2.53	1.43	0.2707		
	CaF ₂ .SiO ₂	2.755×10^{-4}	1	2.755×10^{-4}	7.25	0.0175		
	TiO ₂ .SiO ₂	6.046×10^{-3}	1	6.046×10^{-3}	3.42	0.9550		
	CaO.CaF ₂ .TiO ₂	0.83	1	0.83	3.72	0.0561		
	CaO.CaF ₂ .SiO ₂	5.04	1	5.04	2.85	0.1351		
	CaO.TiO ₂ .SiO ₂	1.26	1	1.26	0.72	0.4255		
	CaF ₂ .TiO ₂ .SiO ₂	1.70	1	1.70	0.96	0.3595		
	Residual	12.36	7	1.77				
Manganese	Model	0.16	13	0.012	6.15	0.0326	Significant	0.89
	Linear Mixture	0.055	3	0.018	1.05	0.4287		
	CaO. CaF ₂	0.042	1	0.042	2.38	0.1671		
	CaO.TiO ₂	2.386×10^{-4}	1	2.386×10^{-4}	8.37	0.0163		
	CaO.SiO ₂	4.33×10^{-3}	1	4.33×10^{-3}	7.58	0.0274		
	CaF ₂ .TiO ₂	1.948×10^{-3}	1	1.948×10^{-3}	0.11	0.7486		
	CaF ₂ .SiO ₂	5.65×10^{-5}	1	5.65×10^{-5}	3.2×10^{-3}	0.9563		
	TiO ₂ .SiO ₂	5.129×10^{-3}	1	5.129×10^{-3}	6.39	0.0308		
	CaO.CaF ₂ .TiO ₂	7.341×10^{-3}	1	7.341×10^{-3}	6.83	0.0261		
	CaO.CaF ₂ .SiO ₂	0.027	1	0.027	1.55	0.2528		
	CaO.TiO ₂ .SiO ₂	2.053×10^{-3}	1	2.053×10^{-3}	0.12	0.7422		
	CaF ₂ .TiO ₂ .SiO ₂	0.012	1	0.012	0.69	0.4336		
	Residual	0.12	7	0.018				
Silicon	Model	0.010	13	7.755×10^{-4}	5.87	0.03949	Significant	
	Linear Mixture	4.846×10^{-3}	3	1.615×10^{-3}	7.94	0.01326		
	CaO. CaF ₂	1.775×10^{-4}	1	1.775×10^{-4}	0.29	0.6081		
	CaO.TiO ₂	4.464×10^{-6}	1	4.464×10^{-6}	7.24×10^{-3}	0.9346		
	CaO.SiO ₂	3.295×10^{-5}	1	3.295×10^{-5}	0.053	0.0237		
	CaF ₂ .TiO ₂	2.872×10^{-5}	1	2.872×10^{-5}	0.047	0.8352		

	CaF ₂ .SiO ₂	2.986x10 ⁻⁴	1	2.986x10 ⁻⁴	5.32	0.0417		0.92
	TiO ₂ .SiO ₂	5.312x10 ⁻⁴	1	5.312x10 ⁻⁴	5.07	0.0452		
	CaO.CaF ₂ .TiO ₂	2.772x10 ⁻⁵	1	2.772x10 ⁻⁵	0.045	0.8381		
	CaO.CaF ₂ .SiO ₂	6.989x10 ⁻⁴	1	6.989x10 ⁻⁴	6.19	0.0322		
	CaO.TiO ₂ .SiO ₂	6.324x10 ⁻⁴	1	6.324x10 ⁻⁴	6.03	0.0344		
	CaF ₂ .TiO ₂ .SiO ₂	1.94x10 ⁻⁷	1	1.94x10 ⁻⁷	5.51	0.0412		
	Residual	4.313x10 ⁻³	7	6.616x10 ⁻⁴				
Hardness	Model	2566.85	9	285.21	5.17	0.02374	Significant	0.90
	Linear Mixture	230.36	3	76.79	4.79	0.03123		
	CaO. CaF ₂	164.14	1	164.14	0.90	0.3624		
	CaO.TiO ₂	307.33	1	307.33	6.31	0.01783		
	CaO.SiO ₂	101.95	1	101.95	0.56	0.4697		
	CaF ₂ .TiO ₂	95.87	1	95.87	0.53	0.4829		
	CaF ₂ .SiO ₂	639.77	1	639.77	3.52	0.0874		
	TiO ₂ .SiO ₂	947.59	1	947.59	5.21	0.0433		
	Residual	181.80	11	181.80				
	Cor Total		20					
Phosphorus	Model	9.28 E-5	13	7.14 E-6	12.7	0.0392	Significant	0.75
	Linear	4.30 E-5	3	1.43 E-5	25.5	0.0138		
	CaO. CaF ₂	3.10 E-6	1	3.10 E-6	5.58	0.0482		
	CaO.TiO ₂	2.10 E-5	1	2.10 E-5	3.73	0.0947		
	CaO.SiO ₂	1.07 E-5	1	1.07 E-5	19.1	0.0208		
	CaF ₂ .TiO ₂	7.61 E-7	1	7.61 E-7	0.14	0.7238		
	CaF ₂ .SiO ₂	4.85 E-6	1	4.85 E-6	8.67	0.0384		
	TiO ₂ .SiO ₂	2.08 E-5	1	2.08 E-5	3.70	0.0959		
	CaO.CaF ₂ .TiO ₂	7.01 E-6	1	7.01 E-6	12.55	0.0301		
	CaO.CaF ₂ .SiO ₂	1.40 E-6	1	1.40 E-6	0.251	0.6330		
	CaO.TiO ₂ .SiO ₂	1.11 E-5	1	1.11 E-5	19.80	0.0202		
	CaF ₂ .TiO ₂ .SiO ₂	3.92 E-8	1	3.92 E-8	6.97 E-3	0.9358		
	Residual	3.93 E-5	7	5.62 E-8				
Sulphur	Model	1.06 E-4	13	8.15 E-6	7.39	0.0066	Significant	0.93
	Linear	3.75 E-5	3	1.25 E-5	11.32	0.0045		
	CaO.CaF ₂	3.58 E-8	1	3.58 E-8	0.032	0.8622		
	CaO.TiO ₂	2.86 E-5	1	2.86 E-5	25.95	0.0014		
	CaO.SiO ₂	8.86 E-7	1	8.86 E-7	0.80	0.4001		
	CaF ₂ .TiO ₂	9.61 E-6	1	9.61 E-6	8.70	0.0214		
	CaF ₂ .SiO ₂	3.54 E-8	1	3.54 E-8	0.032	0.8629		
	TiO ₂ .SiO ₂	3.31 E-7	1	3.31 E-7	0.30	0.6008		
	CaO.CaF ₂ .TiO ₂	3.83 E-6	1	3.83 E-6	3.48	0.1046		
	CaO.CaF ₂ .SiO ₂	6.04 E-7	1	6.04 E-7	0.55	0.4835		
	CaO.TiO ₂ .SiO ₂	2.79 E-6	1	2.79 E-6	2.53	0.1557		
	CaF ₂ .TiO ₂ .SiO ₂	1.75 E-6	1	1.75 E-6	1.59	0.2478		
	Residual	1.10 E-6	7	1.10 E-6				
Molybdenum	Model	4.10 E-3	13	3.15 E-4	1.04	0.0045	Significant	0.85
	Linear	1.58 E-3	3	5.29 E-4	4.61	0.2456		
	CaO.CaF ₂	7.52 E-4	1	7.52 E-4	2.47	0.0015		
	CaO.TiO ₂	3.39 E-5	1	3.39 E-5	0.11	0.7483		
	CaO.SiO ₂	3.36 E-4	1	3.36 E-4	3.75	0.0321		
	CaF ₂ .TiO ₂	2.65 E-4	1	2.65 E-4	0.87	0.3817		
	CaF ₂ .SiO ₂	1.12 E-5	1	1.12 E-5	0.037	0.8529		
	TiO ₂ .SiO ₂	2.46 E-5	1	2.46 E-5	0.081	0.7841		
	CaO.CaF ₂ .TiO ₂	1.51 E-4	1	1.51 E-4	0.49	0.0045		
	CaO.CaF ₂ .SiO ₂	6.78 E-4	1	6.78 E-4	2.23	0.1790		
	CaO.TiO ₂ .SiO ₂	4.73 E-4	1	4.73 E-4	1.55	0.2575		
	CaF ₂ .TiO ₂ .SiO ₂	4.41 E-4	1	4.41 E-4	1.45	0.2676		
	Residual	2.13 E-3	7	3.04 E-4				

ANOVA along with model equations helped us to identify the constituents and interactions which have synergistic and anti-synergistic effects on bead properties (Table 5.19).

Table 5.12: Effect of coating constituents on physicochemical and thermophysical properties

Interaction	Constituent	C	Si	Ni	Cr	Mn	Hv	P	S	Mo
Individual	CaO	0	-	+	0	0	0	+	-	0
	CaF ₂	0	0	+	0	0	0	+	+	0
	TiO ₂	0	0	+	0	0	0	+	-	0
	SiO ₂	0	+	+	0	0	+	+	0	0
Binary	CaO. CaF ₂	+	0		+	0	0	-	0	+
	CaO.TiO ₂	-	0		+	+	-	-	-	0
	CaO.SiO ₂	0	-		0	-	0	-	0	-
	CaF ₂ .TiO ₂	-	0		0	0	0	0	+	0
	CaF ₂ .SiO ₂	0	+		-	0	0	0	0	0
	TiO ₂ .SiO ₂	0	-		0	+	+	0	0	0
Tertiary	CaO.CaF ₂ .TiO ₂	+	0		0	-	0	0	0	-
	CaO.CaF ₂ .SiO ₂	0	-		0	0	0	0	0	0
	CaO.TiO ₂ .SiO ₂	0	+		0	0	0	+	0	0
	CaF ₂ .TiO ₂ .SiO ₂	0	+		0	0	0	0	0	0

[+: Synergistic, - : Anti Synergistic, 0: No effect]

The predicted versus actual plots for the multi pass bead on plate for weld chemistry and microhardness is presented in Figure 5.19.

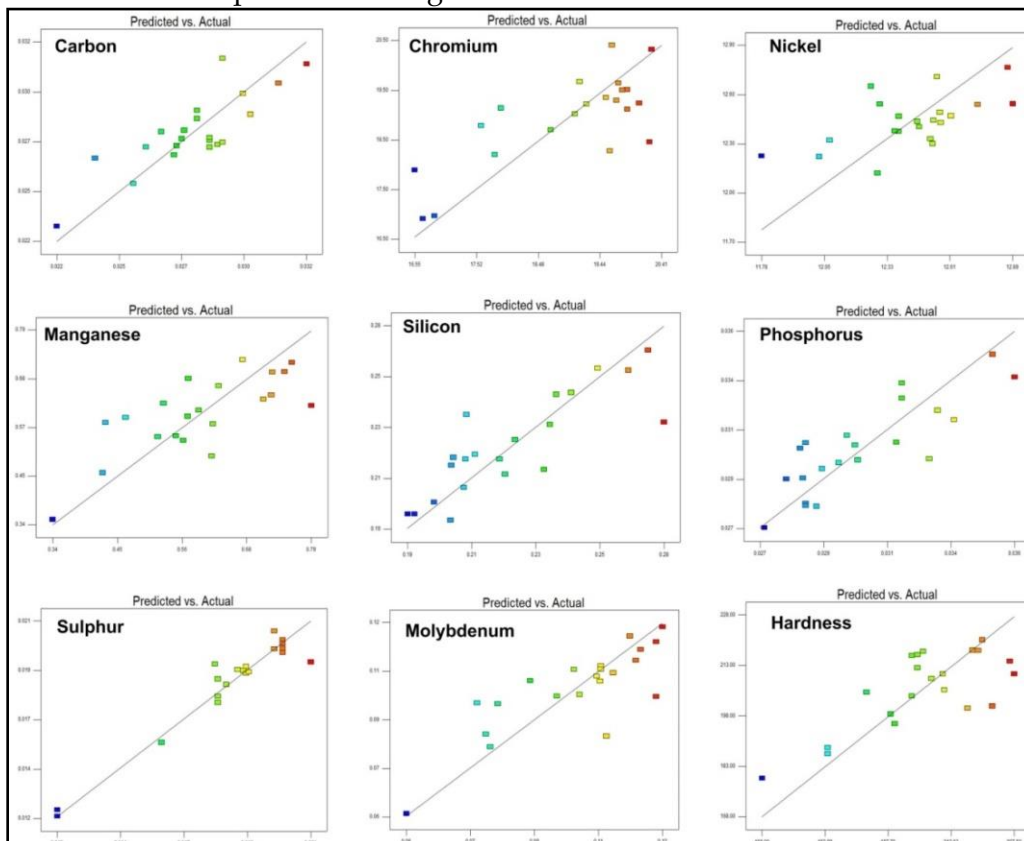


Figure 5.19: Predicted versus Actual plots for weld bead chemistry and properties

Based on the regression model, it is visible that the coating constituent minerals affect the weld chemistry significantly. Individual constituents, as well as their interactions in binary and

tertiary combinations, affect the mechanical behavior of weld by influencing the weld chemistry. It is always desirable that weld should have carbon content lower than the base metal and filler wire. Basicity of the flux has a direct relationship with the amount of oxygen present in the weld. This oxygen is mainly responsible for carrying the carbon from weld to the slag. This transfer of carbon takes place through the chemical reaction: $[C] + [O] = CO$. Basicity is directly proportional to the carbon content in the weld. This implies that basic fluxes and their interaction tend to increase the carbon concentration. Here, as per the regression model, the binary interaction of CaO and CaF_2 along with tertiary interaction $CaO.CaF_2.TiO_2$ increase the carbon content in weld whereas interactions $CaO.TiO_2$ and $CaF_2.TiO_2$ have an anti-synergistic effect on carbon. The p value of model is 0.0451 and lies in the acceptable range of 95% confidence level. Silicon content in the weld increases with the increased input of SiO_2 in the electrode coating. Silicon usually comes in weld metal from the decomposition of coating constituent silica which occurs through following chemical reaction: $SiO_2 = Si + O_2$. Another possible source of Si in the weld metal is due to a slag-metal reaction where the Si^{4+} metallic cation from the slag gets reduced at the molten pool-slag interface and produces Si in the weld. This occurs by the reaction: $Si^{4+} + 4e^- = Si$. The binary interaction of $CaO.SiO_2$ has an anti-synergism effect and that is possibly due to the reduced activity of the SiO_2 by CaO which progresses through the following chemical reaction and forms a complex SiO_4^{4-} : $CaO = Ca^{2+} + O^{2-}$; $SiO_2 + 2O^{2-} = SiO_4^{4-}$. Nickel concentration in the weld progresses linearly as per the developed regression model and is directly proportional to the concentration of each individual constituent of coating mixture. Chromium is yet another important constituent of the weld which enhances the pitting corrosion resistance. The developed regression model shows that the binary mixture of $CaO.CaF_2$, $CaO.TiO_2$ have synergistic effect on chromium content, whereas $CaF_2.SiO_2$ tends to decrease the chromium concentration of the weld deposit. E309L is a high chromium filler wire, but the chromium concentration of welds is always lower than filler. This is mainly due to the availability of oxygen from the disassociation of SiO_2 . The oxygen released from the dissociation of SiO_2 oxidizes chromium to chromium oxide. The main source of manganese in the weld pool is filler wire which is around 1.8% by weight. The coating constituent minerals silica, rutile, calcite, and fluorspar are devoid of manganese hence they do not contribute directly to the presence of manganese in the weld. But their activity and chemical reactions taking place at slag-pool interface affect the manganese concentration significantly. The special cubic model for manganese is significant with its p-value of 0.0326 lying well under the 95% acceptable confidence level. Microhardness is an important mechanical property which ensures enhanced structural integrity of the structure. Quadratic regression model suggests that the binary mixture of $CaO.TiO_2$ and $TiO_2.SiO_2$ have a synergism effect on the micro-hardness. The components including CaF_2 appear to have an anti-synergism effect which is mainly due to the formation of HF (hydrogen fluoride) gas by the interaction of fluorspar with the hydrogen at the molten metal interface. HF is known to deteriorate the hardness of structure. CaO with its desulphurization property contributes significantly in the enhanced hardness. Phosphorus and sulphur are harmful contents of the weld and often referred to as impurities. It is desirable to have its presence in lower amounts. Increased phosphorus content in welds contributes towards enhancing its cracking susceptibility. Similarly, calcite in the weld zone is known to decrease the sulphur content of the weld zone. CaO reacts with sulphur present in welds and forms calcium sulphide, releasing oxygen in the process $[CaO + S = CaS + \frac{1}{2}O_2]$. The regression model indicates that CaF_2 coming from fluorspar tends to increase the sulphur content in the weld. Hence calcium contributes differently towards sulphur concentration when it is bonded with fluorine and oxygen. Similar behavior is depicted by rutile too, where Ti reacts with sulphur to form titanium sulphide (TiS) and releasing oxygen in the process. The presence of sulphur in increased amount enhances the formation of ferrite in the weld zone, which further leads to decreasing the hardness, tensile strength and notch toughness considerably. Sulphur is known to exert its influence through non-metallic inclusions, whereas phosphorus establishes its effect by ferrite strengthening. Molybdenum has strong affinity oxygen and is known to form stable

oxides. Molybdenum is also known to enhance corrosion resistance. Hence along with chromium, it is always desirable to have a good presence of molybdenum in the weld zone of offshore structures. The contour plots for each of the above discussed weld chemistry elements and microhardness is shown in Figure 5.20. Contour plot provides fair estimation of different output of each property expected over the varying coating constituent composition.

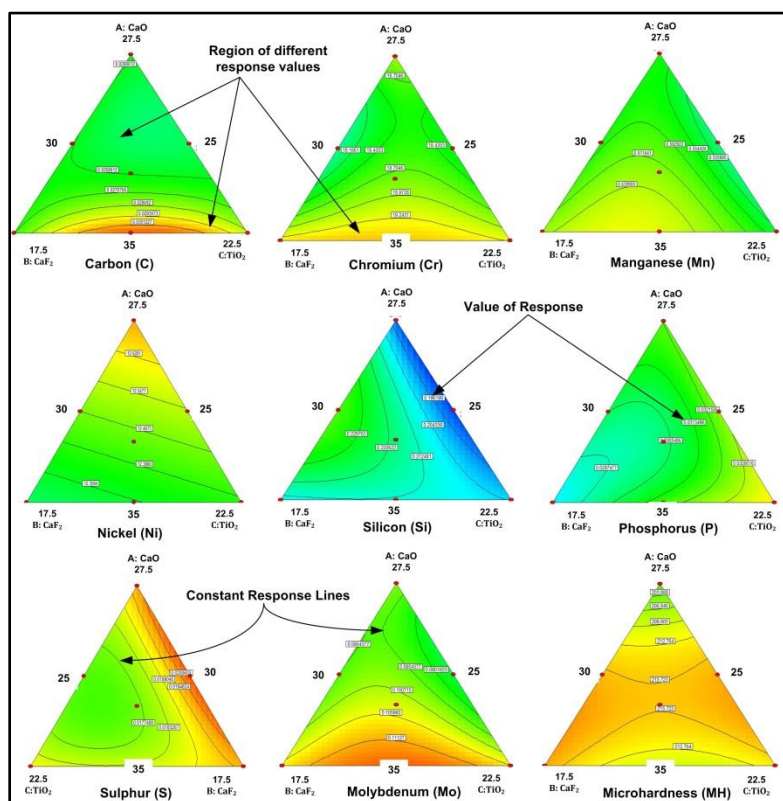


Figure 5.20: Contour plots for bead properties

The developed regression models were further validated by calculating the error percentage between the experimental and model values for all properties, three electrode coating compositions chosen at random from the design matrix. The experimental results and model values were obtained for each of these compositions characterized for different properties. The results of the same is represented in Table 5.13 which shows that %error for all the properties lies below or around 5%, which is in the acceptable limit, validating the model.

Table 5.13: Model validation for deposited bead properties

				Predicted value			Actual Value			%Error		
CaO	CaF ₂	TiO ₂	SiO ₂	C	Si	Ni	C	Si	Ni	C	Si	Ni
30	24.5	25.5	10	0.0274	0.261	12.58	0.0268	0.254	12.42	2.1	2.6	1.6
34	21	29	6	0.0279	0.246	12.36	0.0275	0.268	12.76	1.4	4.8	3.2
31	20	29.5	9.5	0.0259	0.258	12.48	0.0267	0.267	12.11	3.1	3.5	3.1
CaO	CaF ₂	TiO ₂	SiO ₂	Mn	Cr	Hv	Mn	Cr	Hv	Mn	Cr	Hv
30	24.5	25.5	10	0.49	18.35	219.5	0.51	18.79	215.5	4.1	2.3	1.8
34	21	29	6	0.68	19.71	207.7	0.72	19.23	214.6	6.1	2.4	3.3
31	20	29.5	9.5	0.74	19.54	202.6	0.77	19.89	211.2	4.1	1.7	4.3
CaO	CaF ₂	TiO ₂	SiO ₂	P	S	Mo	P	S	Mo	P	S	Mo
30	24.5	25.5	10	0.031	0.013	0.074	0.029	0.012	0.079	6.1	7.6	6.7
34	21	29	6	0.027	0.018	0.117	0.028	0.019	0.111	3.7	5.5	5.1
31	20	29.5	9.5	0.036	0.021	0.118	0.034	0.022	0.124	5.5	4.7	5.9

[C: carbon, Si: silicon, Ni: nickel, Mn: manganese, Cr: chromium, Hv: microhardness, P:phosphorus, S: sulphur, Mo: molybdenum]

5.3. MULTI RESPONSE OPTIMIZATION

The developed regression models are optimized to find the most suitable coating composition from the chosen design space, which would meet the target goals of optimized properties. A composite desirability optimization method has been adopted in this work to optimize the electrode coating composition for desired physicochemical-thermophysical, wettability properties, along with the weld bead chemistry and microhardness. In this method, a composite desirability function 'D' is used to obtain desired responses from the predicted results. The composite desirability function used here can be expressed mathematically as per the equation 5.1 [Lee et al., 2017].

$$D = \left(\prod_{i=1}^n d_i^{w_i} \right)^{1/\sum w_i} \quad (5.1)$$

Here, d_i represents the desirability of i^{th} response, n is the total number of responses to be optimized, w_i is the weightage of each response. For optimization purpose, the goal was set for each property as maximizing it, minimizing or keeping it in the range between maximum and minimum value. The density is desired to be in intermediate range as the coating with low density upon melting would have greater flow ability and there would be chances of it flowing over to the base metals away from the bead, whereas the coating with high density would not be able to cover the bead completely. Similarly the weight loss should be minimum as it is always desirable to have a thermally stable electrode coating upon exposure to high temperature ranges in the welding process. The value of the enthalpy of fusion is desired to be in range as too high or too low enthalpy of fusion would either way affect the weld adversely. Similarly the ranges of thermal properties was decided so that the coatings can perform their intended task and heat flow from the power source to the molten weld pool through the coated electrode can happen suitably. For wettability properties, the a small contact angle leads to increased wetting of the bead with greater spread area, hence enhanced protection from ambient impurities. The surface tension was kept in the intermediate range and adhesion energy was maximized as it ensures that the contact of solidified coating on weld beads remains in proper position for the desired time. For the weld bead chemistry, chromium and molybdenum are known to increase the pitting resistance equivalent number (PREn), hence their content has to be maximized. Nickel enhances corrosion resistance and silicon favors easy slag detachability, thereby requiring maximized content. Phosphorus and sulphur are weld impurities which also increases susceptibility to solidification cracking and hence, it is desirable to have their presence in the weld bead in minimum quantity.

The optimized solution for the experimented electrode coating properties along with contour plots of solution's desirability is shown in Table 5.14 and Figure 5.21 respectively. The two optimum solutions were obtained with their respective desirability being 65.5% and 62.6% respectively.

Table 5.14: Optimum Solution for physicochemical-thermophysical properties

Sol.	CaO	CaF ₂	TiO ₂	SiO ₂	C	Si	Mn	Cr	Ni	Hv	P	S
1	29.22	22.26	28.50	10.0	0.023	0.261	0.657	19.23	12.52	216.6	0.027	0.014
2	31.03	22.93	26.03	10.0	0.023	0.264	0.641	19.12	12.45	212.8	0.029	0.105
					Mo	ρ	ΔH	ΔW	TC	TD	SH	CA
1	29.22	22.26	28.50	10.0	0.106	1.436	-20247.2	15.75	0.257	0.235	1.086	31.67
2	31.03	22.93	26.03	10.0	0.105	1.450	-21995.6	16.89	0.266	0.238	1.103	46.80
					ST	AE	SA	Desirability				
1	29.22	22.26	28.50	10.0	467.9	0.89	11313	0.655				
2	31.03	22.93	26.03	10.0	471.9	0.85	12878	0.626				

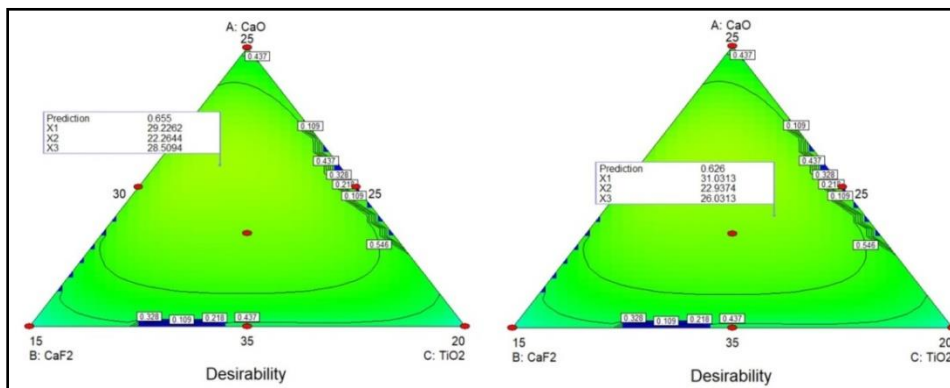


Figure 5.21: Contour plots of optimum solutions' desirability

The two optimum solutions obtained here were used to develop electrode coating and they were also characterized for different properties as that of coating compositions from design matrix, discussed in previous sections. Upon obtaining the property values in suitable ranges, multi pass bead on plate were applied with developed electrodes coated with optimum coating compositions. The multi-pass bead on plate was further characterized qualitatively and quantitatively for deposit chemistry and microhardness. The bead showed similar properties as that of others, and it was further compared with twenty one beads from design matrix for the selection of most suitable electrode coating to fabricate weld. The experimental values obtained for the two optimum solutions are summarized in Table 5.15 below:

Table 5.15: Properties of electrode with optimum solution coatings

Sol.	C	Si	Mn	Cr	Ni	Hv	P	S	Mo	ρ
1	0.025	0.26	0.44	18.78	12.61	212.5	0.028	0.017	0.074	1.42
2	0.024	0.23	0.47	18.11	12.24	205.7	0.025	0.015	0.065	1.43
	ΔH	ΔW	TC	TD	SH	CA	ST	AE	SA	
1	18890.1	14.1	0.291	0.246	1.07	33.5	461.5	0.82	10892	
2	18258.3	14.5	0.242	0.211	1.08	38.6	469.8	0.78	12454	

5.4. SELECTION OF MOST SUITABLE ELECTRODE COATING COMPOSITIONS

A series of extensive characterization of multi pass bead on plate was carried out, involving both the qualitative and quantitative aspects. The electrode's performance was assessed qualitatively by analyzing the smoke produced during welding, slag detachability, ease of arc initiation and arc continuity. The qualitative parameters were marked on a comparative scale of 0-10 for each electrode. The marks between 0-3 were graded as poor performance, 4-7- fair and 8-10 belonged to good category. Ease of arc initiation was compared in terms of re-striking attempts for initiating the arc, whereas slag detachability was compared using three tap test. The continuity of arc during applying of multi-pass beads was used to assess the arc stability. Quantitative analysis was carried out in terms of bead chemistry which has already been discussed in previous section and desirable content for each element. Pitting resistance equivalent number ($PREN = \%Cr + 3.2 \%Mo + 16 \%N$) for each deposited bead was also calculated to assess and compare their performance in corrosive marine environment. The comparative analysis of twenty one beads applied using compositions from design matrix and two using optimum coating compositions is provided below in Table 5.16.

Table 5.16: Comparative assessment for electrode coating performance

Coating	PREn	Slag detachability	Smoke	Ease of arc ignition	Arc stability
1	18.05	Good	Good	Good	Fair
2	17.11	Good	Good	Fair	Fair
3	18.98	Good	Fair	Fair	Fair
4	18.14	Fair	Fair	Fair	Fair
5	16.81	Fair	Fair	Good	Fair
6	16.86	Good	Fair	Fair	Fair
7	17.87	Good	Fair	Fair	Good
8	19.85	Fair	Fair	Good	Fair
9	20.07	Fair	Fair	Fair	Fair
10	20.17	Fair	Fair	Good	Good
11	20.39	Good	Fair	Good	Good
12	19.99	Good	Fair	Good	Good
13	20.07	Good	Fair	Fair	Fair
14	19.94	Fair	Fair	Fair	Good
15	19.46	Good	Good	Fair	Fair
16	19.39	Good	Good	Good	Good
17	20.60	Fair	Fair	Good	Fair
18	20.24	Fair	Fair	Good	Fair
19	20.64	Good	Fair	Fair	Good
20	20.19	Good	Fair	Fair	Fair
21	19.58	Good	Good	Good	Good
O1	19.01	Good	Fair	Fair	Good
O2	18.31	Fair	Good	Fair	Fair

Pitting resistance equivalent number (PREn) is a fair indicator of pitting resistance for a weld supposed to perform in corrosive marine environment. Here based on bead chemistry, PREn was found to vary in the range of 16.81-20.64. In the first assessment, the coating with PREn higher than 19, were shortlisted. The shortlisted coatings were then analyzed for grades awarded to them for qualitative parameters. These considerations were used to select coating 16 and 21 as the most suitable compositions. The coating prepared from optimum composition 1 was found to have a PREn marginally more than 19, but it performed just fairly in terms of smoke and arc ignition. The electrode made of coating compositions 16 and 21 are referred as E16 and E21 in further sections of this thesis. Laboratory developed electrodes E16 and E21 have been used to fabricate a dissimilar weld between super duplex stainless steel 2507 grade and pipeline API X70 steel in section 5.5.

5.5. DISSIMILAR JOINING OF API X70/ SUPER DUPLEX STEEL 2507 BY SMAW PROCESS: FABRICATION & CHARACTERIZATION

Based on results of extensive qualitative and quantitative characterizations performed on multi pass bead on plate in section 5.2 above, electrode coating compositions 16 and 21 were chosen as the most preferred composition for extrusion on 309L filler wire and producing two set of laboratory developed electrodes, referred as E16 and E21 hereafter. Laboratory developed electrodes E16 and E21 were used to fabricate a dissimilar weld between X70 and super duplex stainless steel 2507. Another weld between the same materials was fabricated using commercially available 309L coated electrode, referred to as E309L hereafter. The three welds were then characterized for mechanical, metallurgical, corrosion and tribological properties. A comparative analysis of these three welds was then done to ascertain the performance appropriateness of the laboratory developed electrodes. The schematic shown in Figure 5.22 describes the experimentation performed in this section.

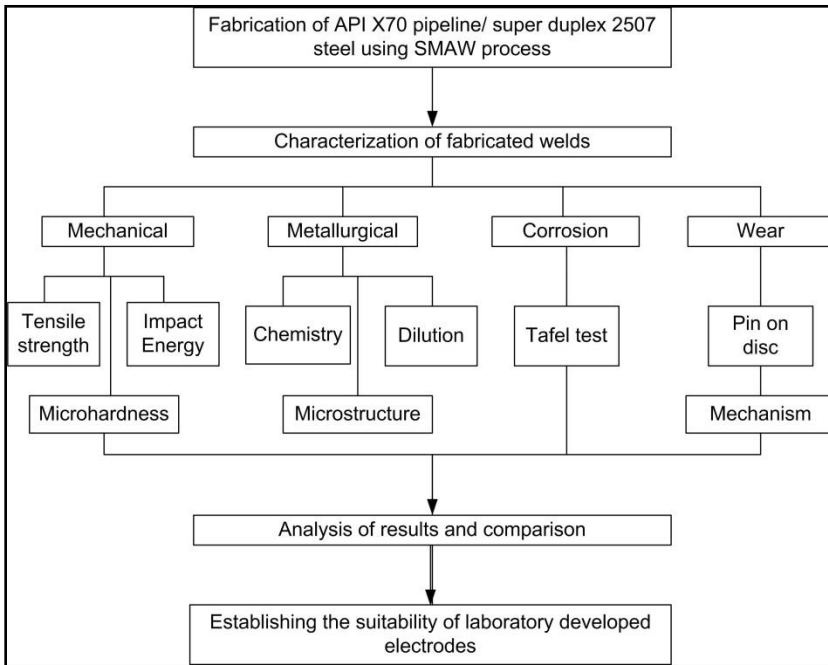


Figure 5.22: Schematic of SMAW weld fabrication and characterization

5.5.1. WELD GEOMETRY & PARAMETERS

Both the base metals were procured in the dimension of 290x290x15 mm plates. Coupons of dimension 250x70x15 mm were prepared from base metal plates, whose edge was machined to an angle of 30° each to obtain a single V groove of 60° with 3mm root gap. Figure 5.23 presents the weld geometry along with sample characterization plan. The welding parameters used for fabrication of weld are summarized in Table 5.17. The average heat input for each filling passes was maintained at approximately 0.275 kJ/mm.

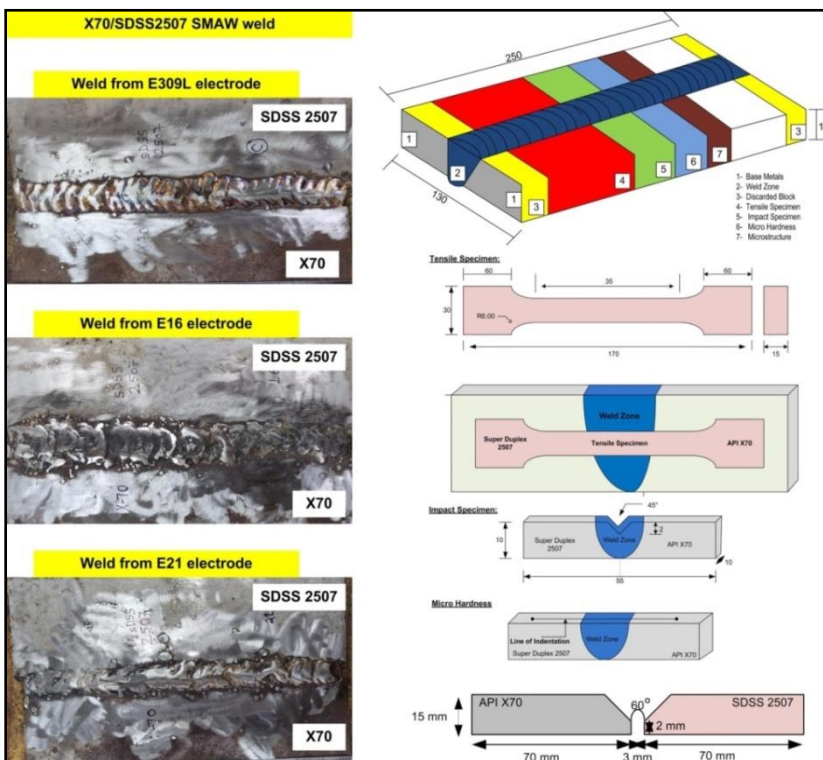


Figure 5.23: SMAW weld geometry and characterization plan

Table 5.17: SMAW weld parameters

Location	Process	Filler	Current (I) (Amperes)	Voltage (V), (Volts)
Root	GTAW	309L (2.1 mm)	90	20
Filling	SMAW	309L coated electrode (3.15 mm)	110	25
Cap	SMAW	309L coated electrode (3.15 mm)	110	25

The macrograph of deposited welds as observed in cross section under stereomicroscope is shown in Figure 5.24.

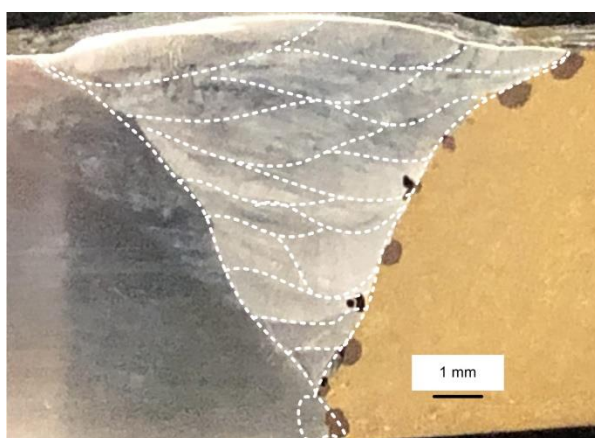


Figure 5.24: Macrograph of weld deposition

5.5.2. MECHANICAL CHARACTERIZATION OF WELDS

The welds fabricated using the three electrodes (E309L, E16, and E21) were characterized for mechanical properties of ultimate tensile strength, impact energy, and microhardness under similar testing conditions. Three specimen of each type were tested for tensile properties. The average tensile properties of base metals and weld joints obtained from the three electrodes are summarized in Table 5.18. The fractured tensile specimen is shown in Figure 5.25.

Table 5.18: Tensile properties of welds and base metals

Specimen	Type	Ultimate Tensile Strength (N/mm ²)	Mismatch with X70	Mismatch with SDSS	%Elongation
X70	Base Metal	602.12 ± 10	-	-	20.11
SDSS 2507	Base Metal	820.65 ± 8	-	-	40.41
E309	Commercial Electrode	662.54 ± 14	1.10	0.81	28.23
E16	Developed Electrode	639.81 ± 18	1.06	0.77	30.51
E21	Developed Electrode	615.61 ± 10	1.02	0.75	28.37

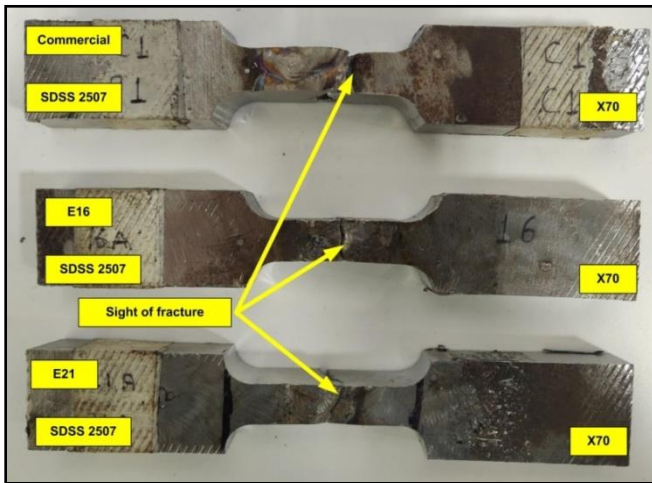


Figure 5.25: Fractured tensile specimen of SMA welds

The fractograph of weld specimens at high magnification obtained using scanning electron microscopy is presented in Figure 5.26. The weld fracture zone has a mix of dimples, ductile dimples, cleavage facets, and tear ridges. The cleavage facet is a low-energy fracture that propagates along the cleavage plane, and it is symmetrically flat with the matching faces [Pandey et al., 2017; Thakare et al., 2019]. The fractured tensile specimens of welds fabricated using commercial and laboratory-developed electrodes here do not have a perfect matching cracked surface, and even the cleavage facets on images are comparatively in lower proportions. This implies cleavage fracture is not the primary mode here. Weld fabricated with commercial electrodes shows the largest size of dimples on the fractured surface as compared to laboratory-made electrodes. The presence of ductile dimples on E16 and E21 made welds is higher as compared to the commercial electrode. This also confirms the high ductility of welds made with E16 and E21 as compared with that made with the commercial electrode. Transgranular ductile dimples dominate the SEM image of a fractured tensile specimen. Reheating of the weld zone in multi-pass welding leads to grain coarsening and micro void occurrence. The coalescence of micro voids further causes ductile tearing and reduces the presence of cleavage facets.

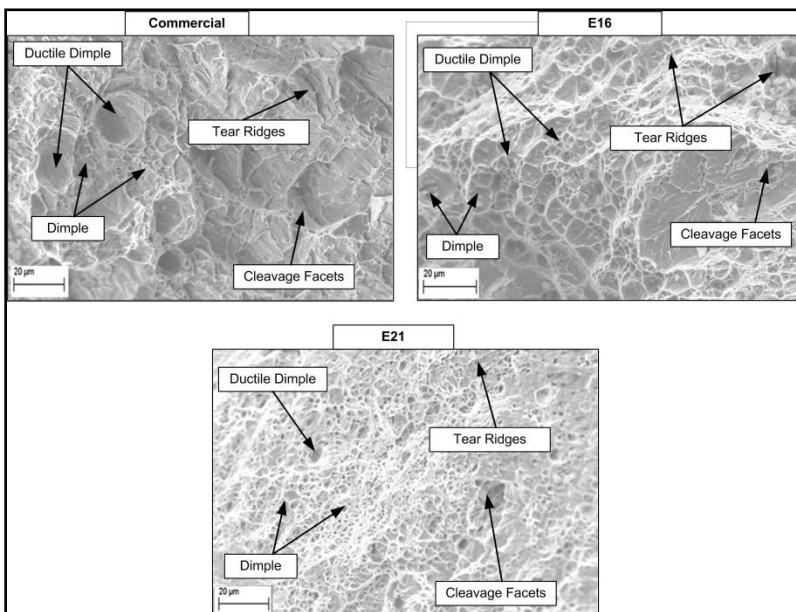


Figure 5.26: Fractograph of weld tensile specimens

Impact strength measurement of base metals and weld zone was done for all the welds. Five specimens for each type were tested. The specimen's highest and lowest values were discarded and the mean value of the three acceptable measurements was chosen for comparison across the

welds and base metals. Results presented in Table 5.19 indicate that welds fabricated with E16 and E21 have better impact strength than those with the commercial electrode. The impact values of weld regions were found to be significantly less than the base metals. However, the impact value of all specimens was above 80J, which is the standardized minimum value required for the qualifying structural integrity of dissimilar welds [Rathod et al., 2015]. A slightly lower impact energy value of E21 can be attributed to fine slag inclusions and their corresponding micro voids. Slag at its local site of inclusion inhibits the proper mixing of molten weld metal and particles binding with each other. Moreover, the inclusions have a lower matrix to particle binding energy, which acts as a favorable site for voids to initiate and for their coalescence, which acts as a deterrent for impact energy. The successive coalescence of these voids further leads to crack and propagation in the direction of lower energy. Moreover, the commercial electrode weld has maximum silicon content compared to E16 and E21. Silicon is known to influence the impact energy adversely. The SEM fractograph of weld's impact specimen shows the presence of micro-cracks, micro-voids and quasi cleavage in the fracture zone. The coalescence of these micro voids is an instrumental reason behind the fracture to occur. At a higher magnification, the dimples showed heterogeneity in size (Figure 5.27).

Table 5.19: Impact Energy of weld and HAZ (J)

Zone	Impact Energy (J)		
	E16	E21	Commercial
Weld Zone	132±5	118±6	110±3
HAZ SDSS side	121±5	112±4	106±4
HAZ X70 side	107±3	101±4	98±3

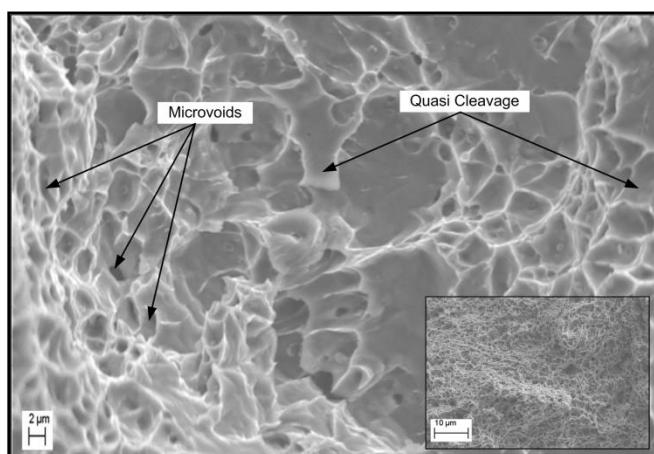


Fig 5.27: Fractured surface appearance of an impact specimen

The microhardness profile of the three welds taken in transverse direction is shown in Figure 5.28. The overall trend of microhardness variation remains similar for the three welds. The hardness of HAZ on the API X70 side is higher than other zones, which may be attributed to the microstructural variations along with re-austenization and precipitation of various micro constituents such as carbides. There is a significant difference in chemical composition of weld fusion zone and X70 steel, which makes the elemental segregation across the weld boundary very sharp. This significant difference in chemical composition further leads to increased carbon activity and possibility of carbide precipitation which imparts higher hardness. The hardness followed the trend of E309L > E16 > E21.

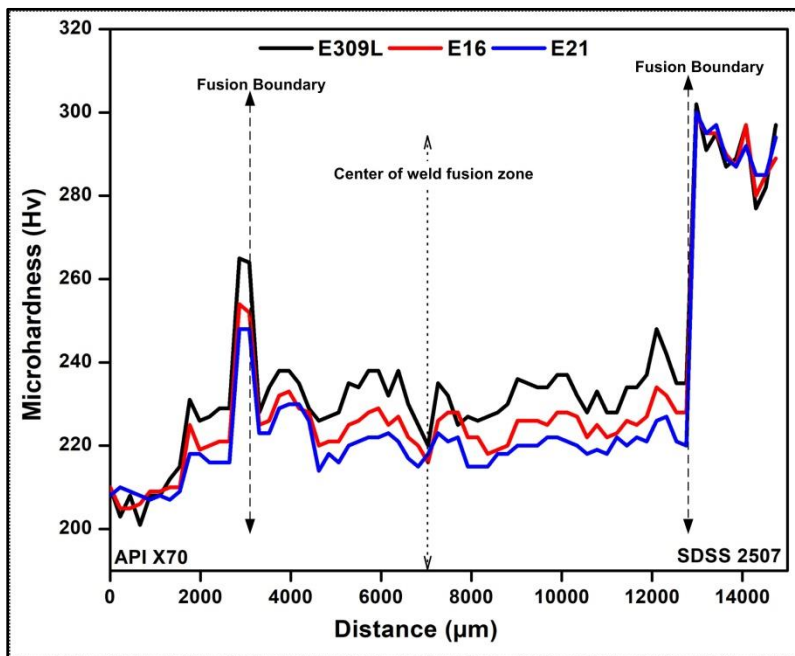


Figure 5.28: Microhardness profile of welds

5.5.3. METALLURGICAL CHARACTERIZATION OF WELDS

The three welds fabricated using laboratory developed electrodes E16, E21, and commercial electrode E309L were subjected to metallurgical characterization which includes solidification mode of filler wire, weld metal chemistry estimation, microstructure characterization of weld fusion zone and heat affected zones. Figure 5.29 below present schematic of work performed in this section.

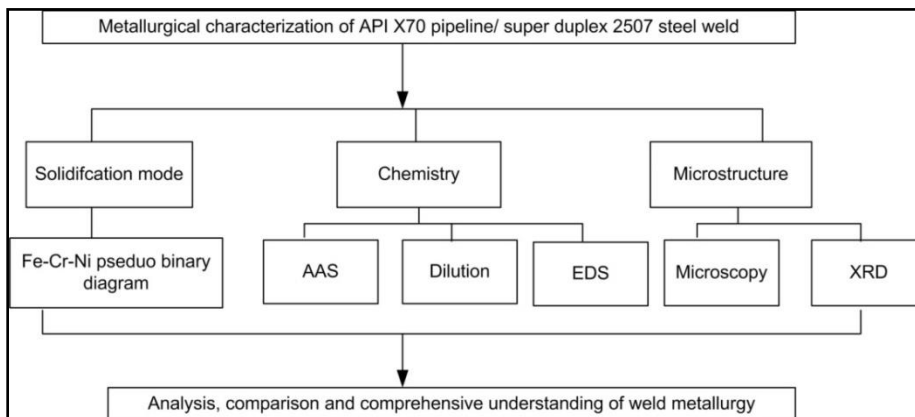


Fig 5.29: Schematic for metallurgical characterization of SMA welds

The microstructure of base metal API X70 steel consists of fine ferrites. It has a discontinuous spread of the pearlite phase. Ferrite grain boundaries also witness precipitation of a few martensite-austenite constituents. The microstructure shows the presence of very fine needle-like polygonal ferrite and bainite. The nucleation of bainite usually occurs at austenitic boundaries and at the apex of bainitic ferrites. The microstructure of base metal super duplex stainless steel 2507 represents a homogenous and equiaxed distribution of austenite and ferrite grains. It has two phases present throughout with austenite grains embedded in the ferrite matrix. The microstructure is devoid of any other significant phase or precipitate (Figure 5.30).

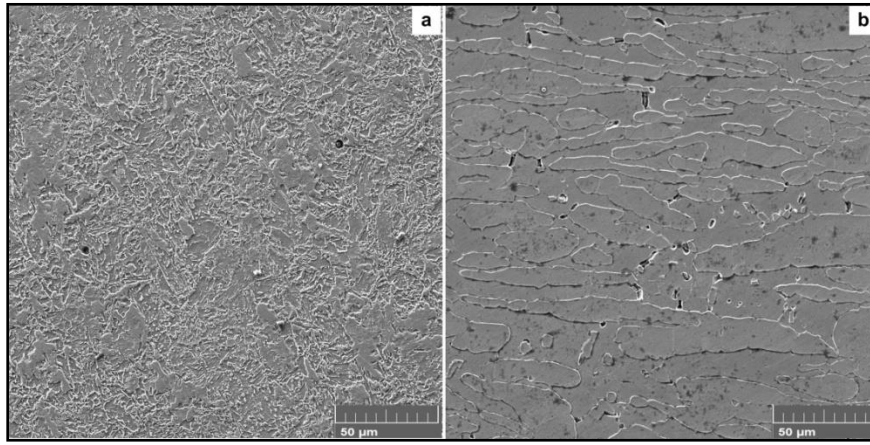


Fig 5.30: Microstructure of base metals: (a) API X70 (b) Super duplex stainless steel 2507

Phase mapping in base metal's XRD confirms the presence of γ and δ phases in the microstructure (Figure 5.31). The γ/δ ratio was found to be 51/49 for super duplex 2507.

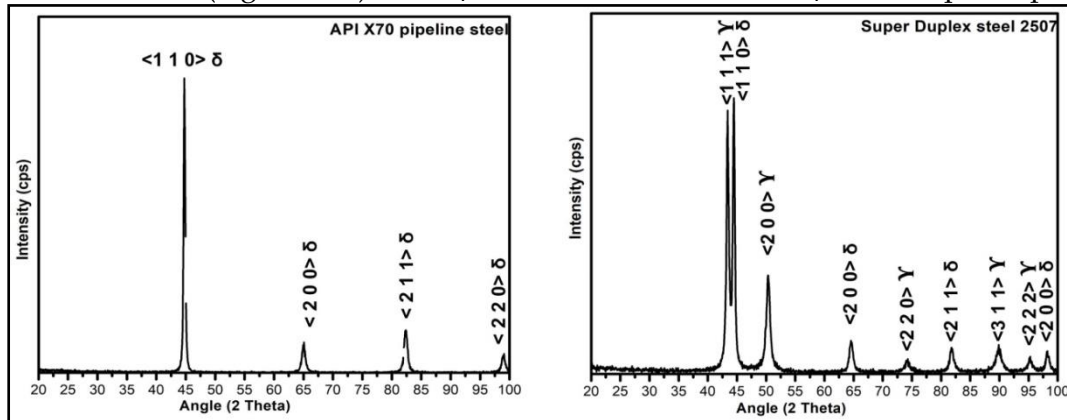


Figure 5.31: XRD of base metal

Fe-Cr-Ni pseudo-binary diagram for filler 309L predicts its solidification in Ferrite-Austenite (F-A) mode with Cr_{eq}/Ni_{eq} being approximately 1.85. The Schaeffler diagram also predicts the chemical composition-based resultant microstructure of the weld zone to be ferrite-austenite (Figure 5.32).

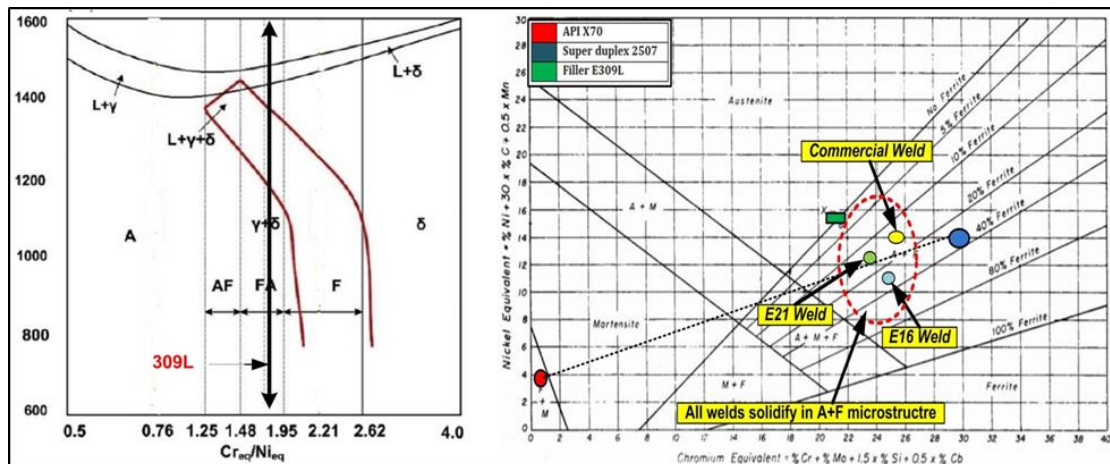


Figure 5.32: Fe-Cr-Ni pseudo binary diagram and Schaeffler diagram plot for the 309L filler and welds

At the end of the solidification process, the peritectic-eutectic reactions drive austenite precipitation at the ferrite solidification boundaries. As the primary ferrite solidifies completely, the austenite formation occurs at the dendrite boundaries and along the ferrite cell. The resultant microstructure consists of interdendritic austenite placed between ferrite dendrites.

The moderate cooling rate in the shielded metal arc welding process and medium Cr_{eq}/Ni_{eq} of 309L filler causes ferrite to be present in skeletal morphology in the final weld microstructure. Skeletal ferrites are characterized by primary ferrite lying at the center area of solidification cells. These cells are surrounded by austenite. The cellular austenite solidifies at the interdendritic region of the dendritic ferrites. The peak tip of the austenite phase has a curvature pointed towards the solid-liquid interface. The formation of austenite and ferrite progresses as per the eutectic reaction. Due to the welding speed, the formation of ferrite dendrites is favored over eutectic products as the molten metal gets pushed out of the coupled zone. Hence the cellular austenite appears distinctively in the microstructure and is often referred to as the divorced eutectic product. The microstructure of weld also reveals that both the austenite and ferrite grow along their preferential growth direction [Inoue et al., 2007]. EDS analysis of weld zone shows that the austenite region is comparatively richer in nickel, whereas ferrite is rich in chromium content. Figure 5.33 presents microstructure and EDS mapping of the weld zone.

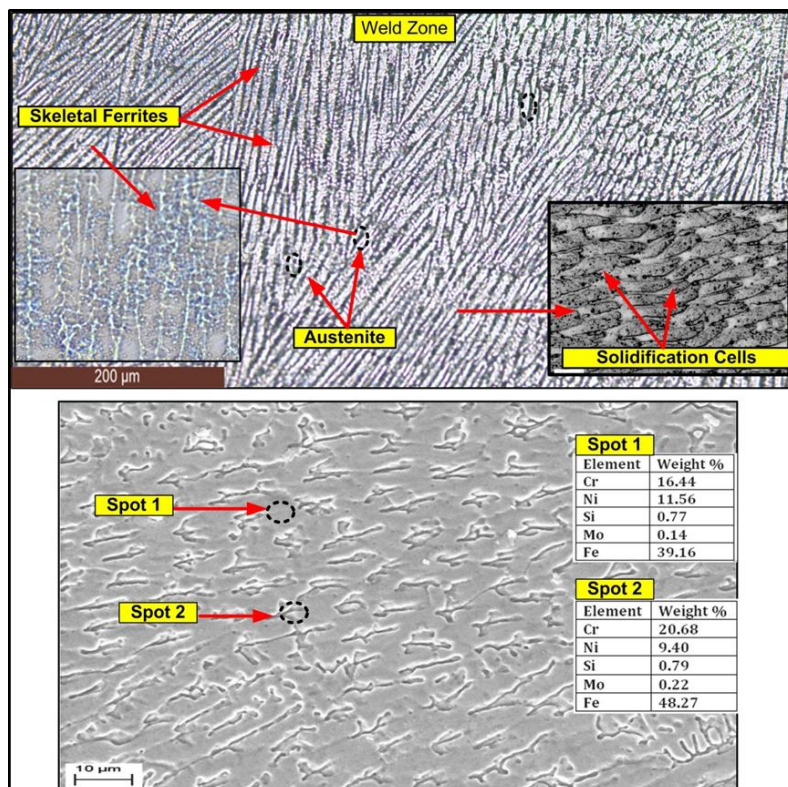


Figure 5.33: Microstructure of weld fusion zone

The microstructure of HAZ on X70 side consists of polygonal ferrite with minor fractions of bainite (Figure 5.34). There is a formation of Type II boundary parallel to the fusion boundary on the X70 side. Type II boundary formed during cooling of molten weld owes its existence to the non-homogeneity between the base and filler metal. The crystal structure of X70 and filler austenitic 309L are different, which causes improper wetting of substrate along the fusion zone. The non-zero contact angle and free energy pose a challenge to the growth of solid at the fusion boundary suppressing the normal epitaxial growth. The partially mixed zone between the fusion line and type II boundary becomes a favorable site for the precipitation of carbides if a significant magnitude of migration occurs from base metal.

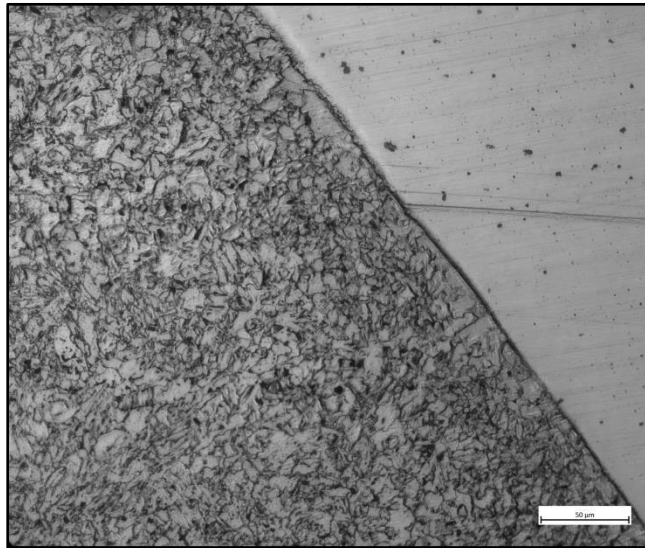


Figure 5.34: Microstructure of heat affected zone on X70 side

The HAZ on the super duplex side represented in Figure 5.35 has ferrite dendrites dominated microstructure. This ferrite transformation is mainly due to the thermal cycle exposure in multi-pass welding, whereas cooling down to room temperature favors the reforming of austenite grains. Columnar dendrites are visible and run almost perpendicular to the weld fusion boundary. The filler and base metal 2507 super duplex both belong to the stainless steel family. In such homogenous welds, competitive continuity of is obtained in the HAZ region between the base metal and weld fusion zone along with grain boundary mismatch. Hence the dendrites in the HAZ region are not in the same orientation as compared to the base metal [Nelson et al., 1999]. The thermal cycles lead to precipitation of primary ferrite and secondary austenite, which minimizes the chances of failure due to hot cracking.

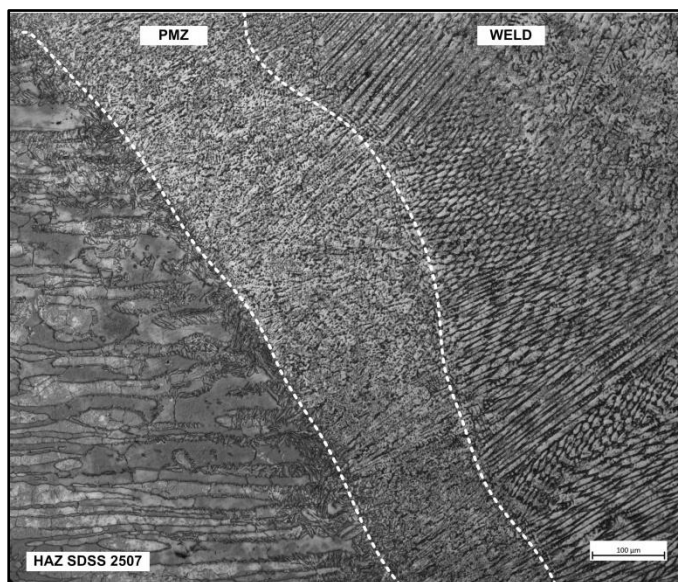


Figure 5.35: Microstructure of heat affected zone on super duplex side

The EDS spectrum of the dissimilar weld was obtained for the regions of base metal, HAZ, and weld zone (Figure 5.36). The significant gradient in the concentration of chromium is observed as we move from super duplex 2507 to X70 steel. X70 being low alloyed steel has a minimal amount of chromium and nickel content. As we move towards the weld zone, there is a steep rise in chromium concentration. The carbon activity between two materials in a dissimilar weld is majorly influenced by carbon and iron content. The partially mixed zone formed between the type II boundary and fusion boundary on the X70 side is an ideal place for carbide dissolution,

and it causes marginal diffusion of carbon from the ferritic steel side. HAZ is the most exposed zone to thermal cycles during multi-pass welding. This region is very susceptible to dissociation and precipitation of carbides, which has the potential to influence the mechanical behavior of weld significantly. The low concentration of chromium and iron in HAZ on the X70 side makes it more susceptible to failure due to corrosion. Manganese shows a reverse trend, where its concentration of decreases as we move from HAZ of X70 to the weld fusion zone further up to the HAZ of the super duplex steel. The nickel concentration in the weld zone and HAZ of super duplex steel is fair enough to impart suitable corrosion resistance. This, along with good chromium concentration, enhances the pitting resistance of the joint. Low nickel concentration on the X70 side and low chromium make this zone prone to failure due to aqueous corrosion.

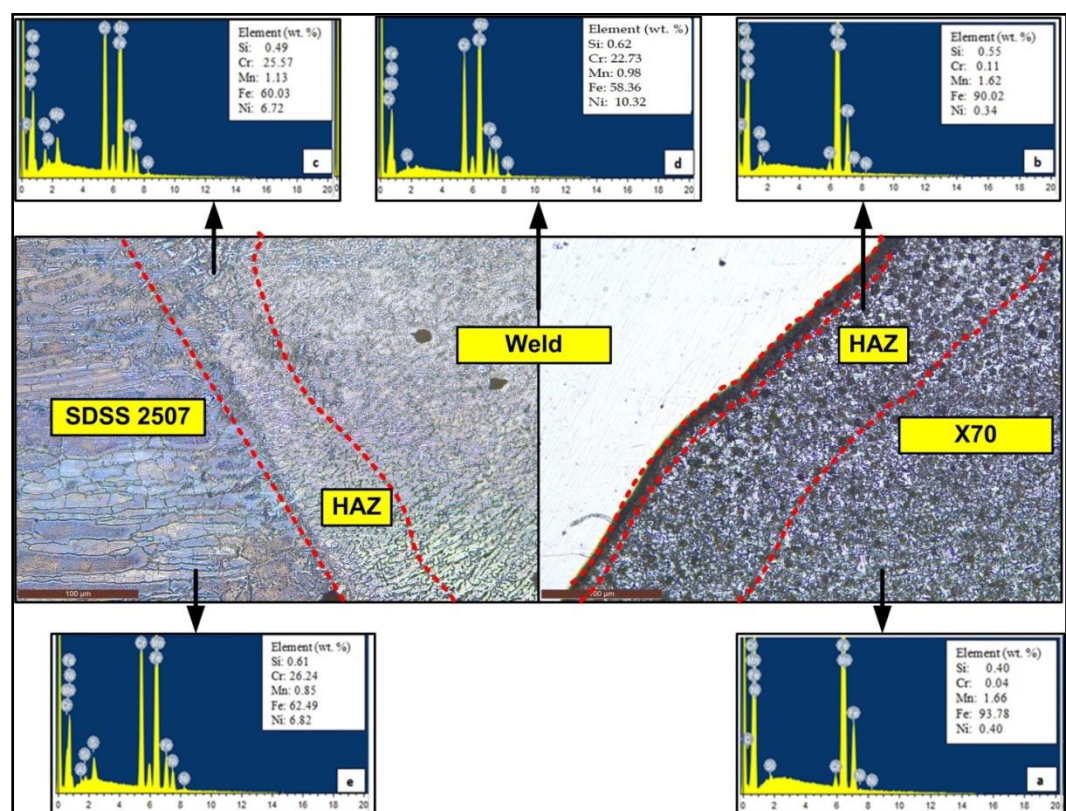


Figure 5.36: Elemental composition in different zones of dissimilar weld made using E309L

The weld fusion zone chemistry was also obtained using atomic absorption spectrometry (AAS). The results of AAS are summarized in Table 5.20 and have been used for equilibrium phase and Scheil's solidification calculations using ThermoCalc software.

Table 5.20: Weld fusion zone chemistry obtained using atomic absorption spectrometer

Electrode/Element	C	Si	Mn	P	S	Cr	Ni	Mo	Fe
E309L	0.038	0.915	0.913	0.031	0.012	24.115	12.632	0.299	59.105
E16	0.044	0.150	0.809	0.045	0.011	23.594	9.354	0.625	69.982
E21	0.029	0.202	0.742	0.039	0.012	22.832	11.087	0.357	66.156

The combined concentration of phosphorus and sulphur (P+S wt.%) was found to be 0.043, 0.056, and 0.051 for E309L, E16, and E21 respectively which indicates high resistance of welds against solidification cracking (Figure 5.37) [Lippold et al., 2005]. A significant difference in silicon concentration is observed in the three welds. It is clearly visible that silicon concentration is highest in E309L weld as compared to laboratory developed E16 and E21 electrode made welds. Silicon concentration is known to positively influence the hardness, hence the resultant microhardness of weld was found to follow sequential order of E309L>E16>E21. The carbon

concentration in the three welds was in comparable range and very low in concentration, which indicates almost similar weldability of the three welds.

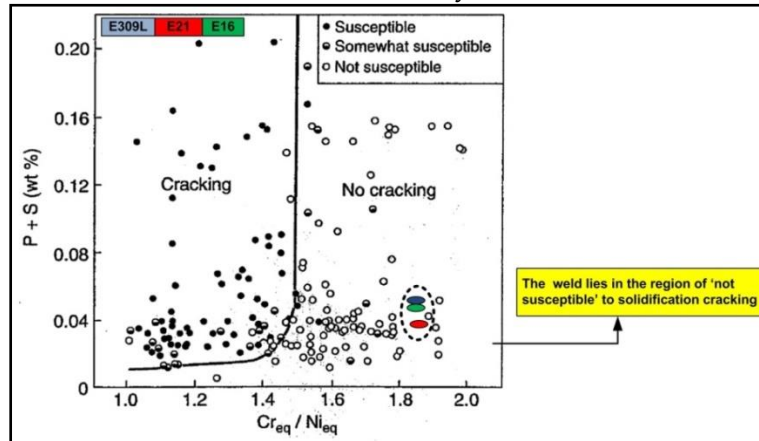


Figure 5.37: Solidification cracking susceptibility of welds based on (P+S wt. %)

The dilution was calculated for each of the three welds, which was found to be 28.5%, 29.2%, and 28.6% respectively for the welds made with E309L, E16, and E21 electrodes respectively. Based on dilution, the weld chemistry was calculated for each weld and the results are summarized in Table 5.21.

Table 5.21: Dilution calculations

Weld	Total Dilution (%)	Weld Chemistry (% wt.)			
		Cr	Ni	Mo	Mn
E309L	28.5	20.98	10.73	0.67	1.60
E16	29.2	20.84	10.20	0.65	1.59
E21	28.6	21.05	10.75	0.68	1.59

Scheil solidification calculation for the three welds is presented in Figure 5.38. The transformation temperatures for the three welds are summarized in Table 5.22. The Scheil solidification calculation shows precipitation of MS and $M_{23}C_6$ in the later stages of solidification, when δ and γ have already precipitated. But due to very low amount of sulphur in weld fusion zone (approx. 0.01% by weight), there is no MS formation occurring in the weld fusion zone. Similarly the solidified weld microstructure is also devoid of any $M_{23}C_6$, due to fast cooling of weld. The weld made with commercial electrode E309L solidifies completely in the temperature drop of nearly 208°C, whereas the solidification of E16 and E21 made weld happens in the temperature drop ranges of 263.3°C and 240.7°C respectively. The deviation in equilibrium and non-equilibrium solidification temperatures for the three welds was found to be 141°C, 168°C and 157°C for the E309L, E16, and E21 made welds respectively.

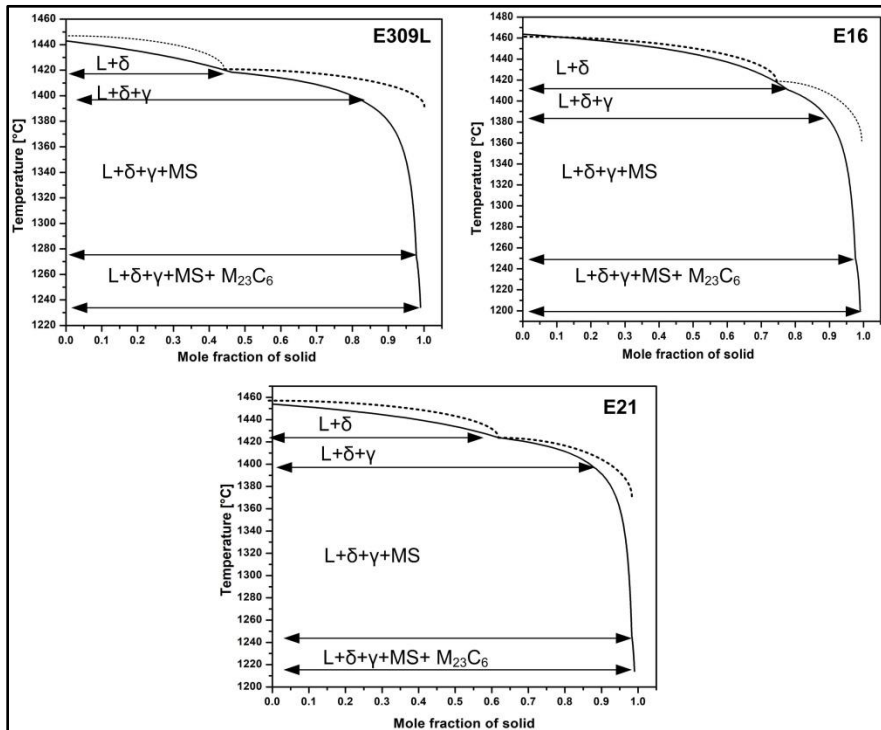


Figure 5.38: Scheil solidification calculation for SMAW welds

Table 5.22: Transformation temperatures calculated using ThermoCalc

Transformation	Temperature (°C)		
	Weld E309L	Weld E16	Weld E21
Liquid starts to transform into primary δ	1442.9	1464.2	1454.1
Start of γ precipitation	1418.2	1412.2	1423.6
Liquid + δ + γ + MS	1394.2	1386.7	1398.4
Liquid + δ + γ + MS + M ₂₃ C ₆	1273.8	1250.2	1245.3
Solidification complete	1234.4	1200.8	1213.4

Similarly the equilibrium phase diagram obtained using ThermoCalc also gives a comparative data for the three welds (Figure 5.39). For the E309L weld, the precipitation of δ starts at around 1417°C, whereas in E16 and E21 welds, the δ precipitation occurs around 1380°C and 1410°C respectively. The γ formation temperature as per equilibrium phase diagram for the three welds is 1392°C, 1367°C, and 1395°C respectively. The phase diagram also shows formation of M₂₃C₆ and M₆C type precipitates, but due to fast cooling of weld and exposure to high temperature for a very short duration of time, they dissolve in the intermediate temperature range and the final weld zone microstructure is devoid of any such carbides.

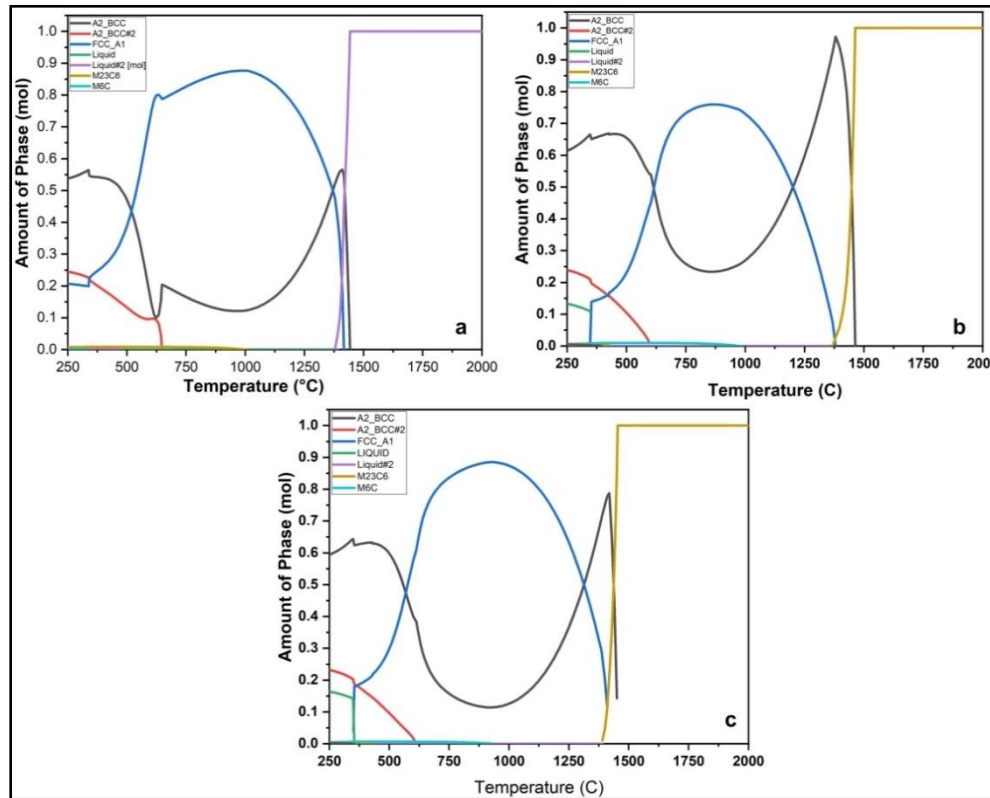


Figure 5.39: Equilibrium phase estimation using ThermoCalc for the SMAW weld made using electrodes: (a) E309L (b) E16 (c) E21

5.5.4. WEAR & CORROSION BEHAVIOR OF SMAW WELDS

The fabricated welds were characterized for wear and corrosion resistance properties. The schematic of wear and corrosion investigations is provided in Figure 5.40 below.

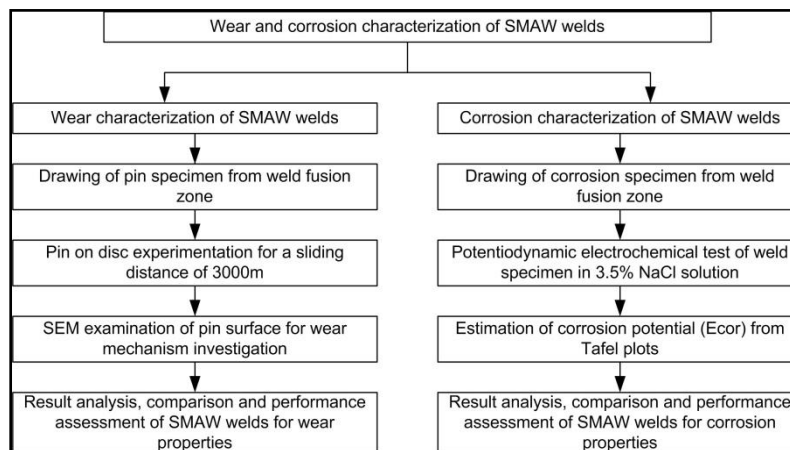


Figure 5.40: Schematic of SMAW weld's wear and corrosion characterization

5.5.4.1. WEAR CHARACTERIZATION

The wear test was conducted using pin on disc method where all weld pin specimen were drawn from the weld fusion zone. The cylindrical pins were made to slide against the bearing steel of E31 grade in dry environment for a sliding distance of 3000m. The results obtained from the wear tests were in accordance with the hardness pattern of the weld presented earlier. Figure 5.41 summarizes the wear (microns), coefficient of friction, and friction force pattern for the three welds fabricated using electrodes E309L, E16, and E21. The mean weight loss for the three welds was found to be 0.1732g, 0.3012g, and 0.3665g respectively for E309L, E16, and E21

electrode fabricated welds. The wear resistance of E309L electrode fabricated weld was found to be superior amongst the three welds under consideration.

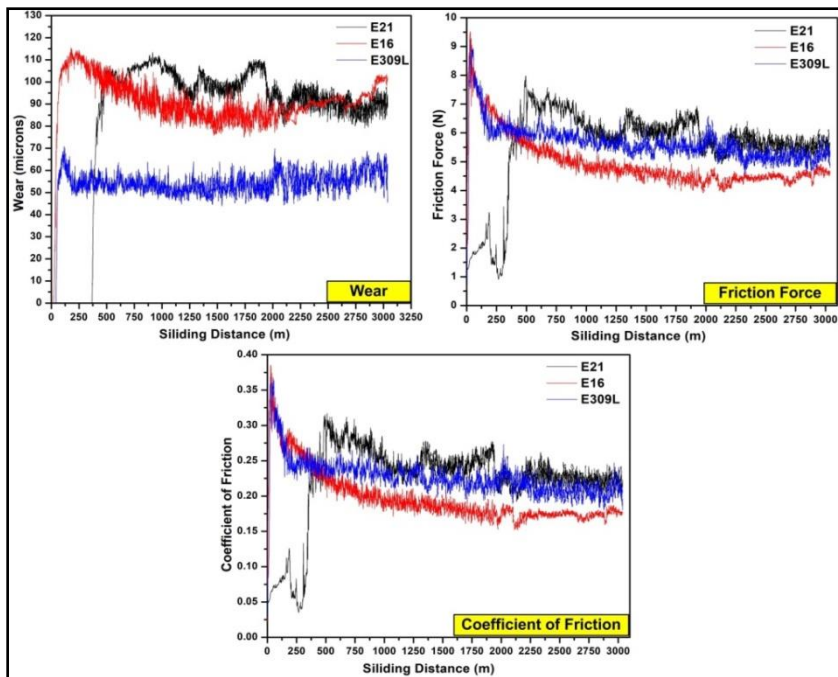


Figure 5.41: Wear results for the SMAW welds

The SEM images of the pin's worn surface was taken at different magnifications and analyzed to ascertain the wear mechanism (Figure 5.42). The mechanism appears to be similar for all the three welds due to uniformity of core wire filler metal and testing conditions. The material appears to be pushed out from the center and a distinctive material break-off can be seen at the edge which breaks the continuity in cross section of the pin's surface boundary. This shows that material removal occurred following ploughing mechanism. Cracks running longitudinally along with material plough indicate abrasive wear. As the sliding distance increases up to 3000m, the crack mature and they appear spalling and flaking coming out of the surface.

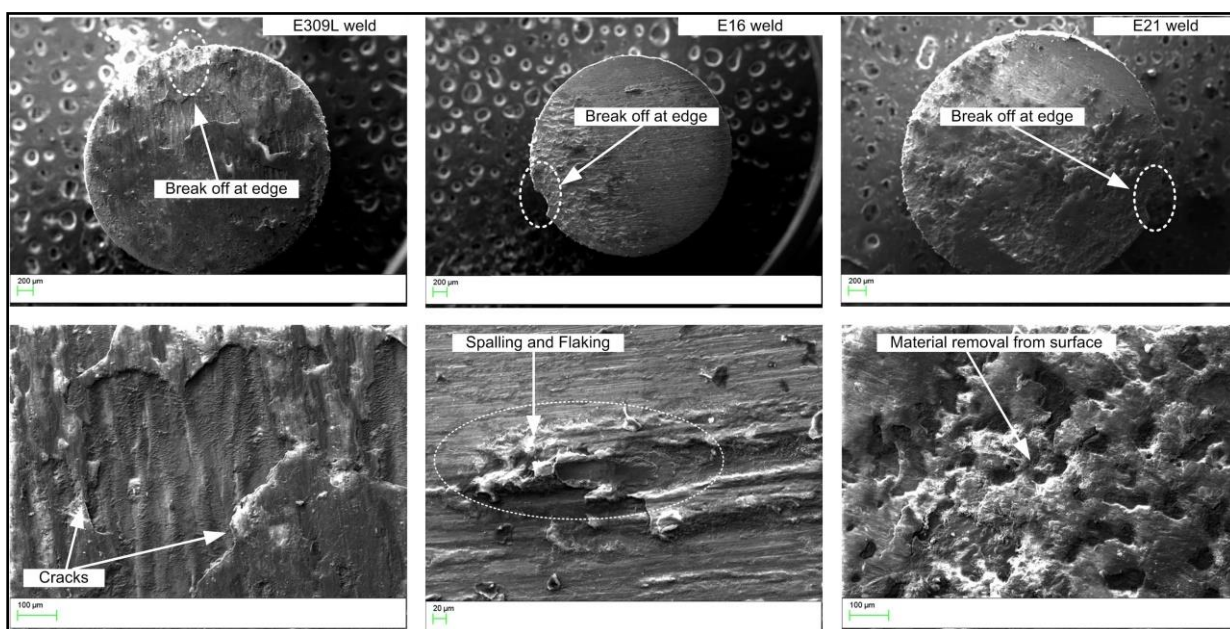


Figure 5.42: Wear mechanism

5.5.4.2. CORROSION CHARACTERIZATION

The electrochemical corrosion of the SMAW welds was conducted in the aqueous environment of 3.5% NaCl solution. The test was performed at a scan rate of 0.167 mV/s in the potential range of -0.25V to +0.25V with reference to the open circuit potential (E_{ocp}). In an electrochemical test, the corrosion potential (E_{corr}) is considered as one of the most sensitive indicator of corrosion resistance. A more negative corrosion resistance means inferior corrosion resistance as compared to that with less negative corrosion potential. Hence, corrosion potential for each of the weld was obtained from the tafel plot. E_{corr} for the three welds was found to be in almost similar range, with E_{corr} of laboratory developed electrode made welds marginally superior to the commercial grade E309L electrode. However, the corrosion resistance of all the three welds was found superior to both the base metals i.e. API X70 and super duplex 2507 steel. This not only justifies the application of such a dissimilar weld but also favors the application of SMAW electrode with said filler wire for the fabrication of the weld. Tafel plots in Figure 5.43 and Table 5.23 below summarize the corrosion results of the two base metals joined in this work and the three welds under investigation.

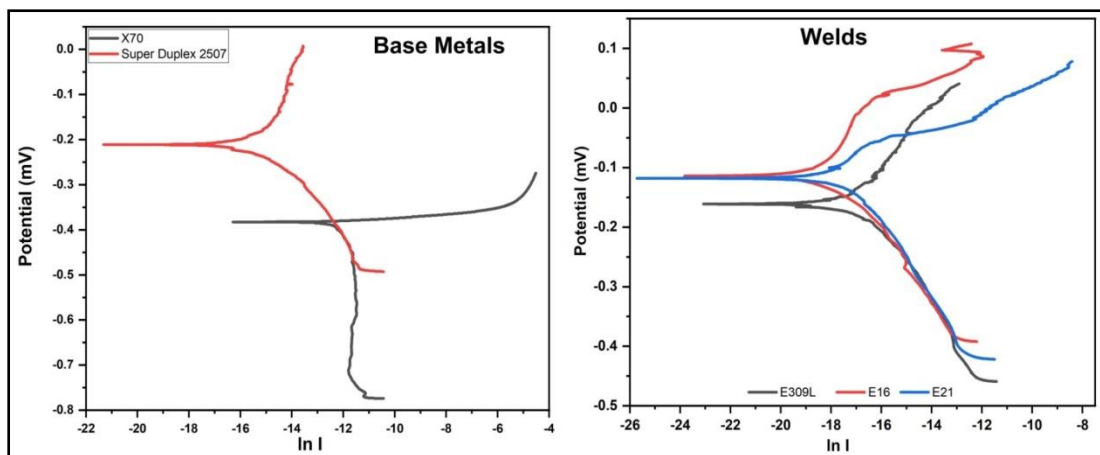


Figure 5.43: Tafel plots for base metals and SMAW process made welds.

Table 5.23: Corrosion potential of base metals and welds

Specimen	Corrosion Potential (E_{corr}) (mV)
API X70 pipeline steel	-382.7
Super Duplex 2507 steel	-211.1
E309L weld	-161.1
E16 weld	-115.9
E21 weld	-117.9

5.6. DISSIMILAR JOINING OF API X70/ SUPER DUPLEX STEEL 2507 BY GTAW PROCESS: FABRICATION & CHARACTERIZATION

A weld joint between API X70 steel and super duplex stainless steel 2507 was fabricated using GTAW process. Two different welds were fabricated employing two candidate filler metals: (i) austenitic 309L (ASS 309L), and (ii) super duplex 2594 (SDSS 2594) at the same heat input. This section discusses the weld geometry, fabrication, metallurgical, corrosion, and mechanical characterization. It is always desirable to weld super duplex stainless steel with matching/overmatching filler to prevent the solidification cracking. Hence, the fillers chosen in this study were from stainless steel family with overmatching Ni and Cr concentration in ASS 309L and SDSS 2594 respectively. A comparative analysis for properties has been provided to

assess the suitability amongst the two candidate filler metals. A schematic of the work performed in this section is provided in Figure 5.44.

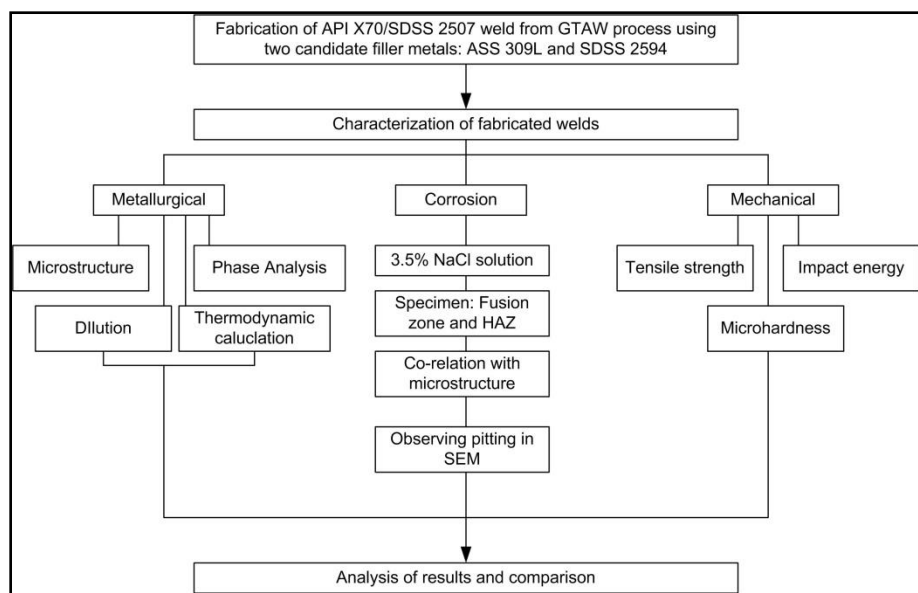


Figure 5.44: Schematic of weld fabrication using GTAW and characterization

5.6.1. WELD GEOMETRY & PARAMETERS

The coupons of dimension 250x70x15 mm were prepared from base metal plates procured originally in the dimension of 290x290x15 mm. The edge of each coupon was machined to an angle of 30° to obtain a single V groove of 60° with 3mm root gap. Figure 5.45 presents the weld geometry along with sample characterization plan. The welding parameters used for fabrication of weld are summarized in Table 5.24. The average heat input for each filling passes was maintained approximately at 0.51 kJ/mm.

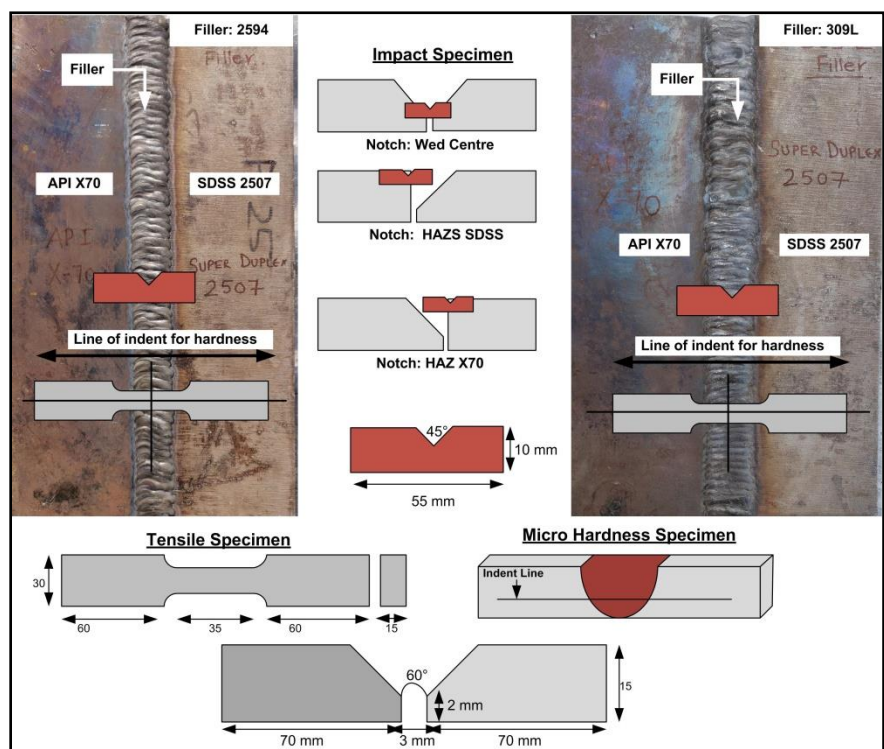


Figure 5.45: GTA weld geometry and characterization plan

Table 5.24: GTAW weld parameters

Location	Process	Filler	Current (I) (Amperes)	Voltage (V), (Volts)	Shielding Gas (l/min)
Root	GTAW	ASS 309L/SDSS 2594 (2.4 mm)	145	15	15
Filler	GTAW	ASS 309L/SDSS 2594 (2.4 mm)	170	15	15
Cap	GTAW	ASS 309L/SDSS 2594 (2.4 mm)	170	15	15

The macrograph of deposited welds as observed in cross section under stereomicroscope is shown in Figure 5.46.

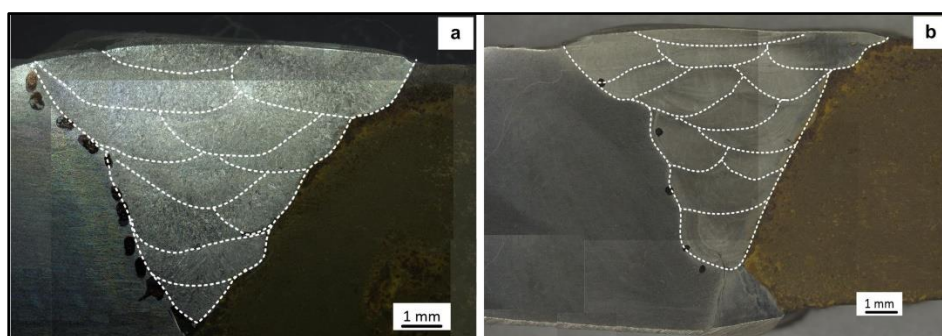


Figure 5.46: Macrograph of weld deposition (a) SDSS 2594 filler (b) ASS 309L filler

5.6.2. METALLURGICAL CHARACTERIZATION OF WELDS

The metallurgical investigation has been performed in a sequential manner, starting from general solidification mode of filler metals to the solidified microstructure. The geometry of weld fusion zone has been estimated using EDS and dilution calculations. The final weld microstructure along with HAZs has been studied using optical microscopy (OM) and scanning electron microscopy (SEM). Rietveld refinement of XRD plots has been done to verify the structural phases present in the weld fusion zone and to estimate the phase fraction. ThermoCalc software has been used to perform thermodynamic calculation for Scheil's solidification and estimation of phases at the equilibrium. The general solidification mode of fillers was estimated based on their Cr_{eq} and Ni_{eq} using Fe-Cr-Ni pseudo binary diagram. The result summarized in Figure 5.47 below clearly indicates that the general solidification mode of filler metal ASS 309L with Cr_{eq}/Ni_{eq} of 1.73 is F-A (ferrite-austenite), whereas for SDSS 2594, Cr_{eq}/Ni_{eq} being 2.28, falls in the range of F (ferritic) solidification mode (Equation 5.2 and 5.3) [Kirschener et al., 1996]. Although the actual solidification of weld fusion zone and solidified microstructure differs due to rapid cooling of the weld below the solvus temperature.

$$Cr_{eq} = Cr + 1.5Mo + 1.5W + 0.48Si + 2.3V + 1.75Nb + 2.5Al \quad (5.2)$$

$$Ni_{eq} = Ni + Co + 0.1Mn + 0.01Mn^2 + 18N + 30C \quad (5.3)$$

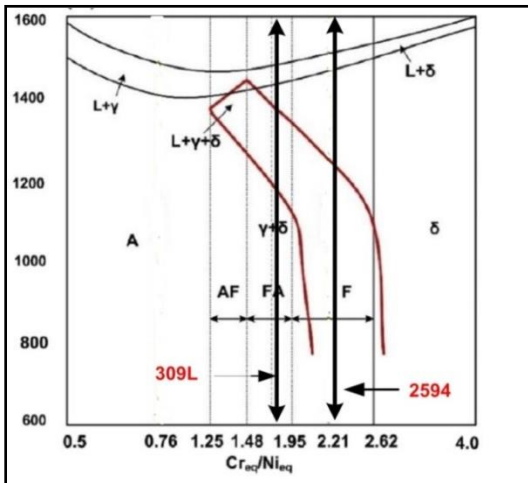


Figure 5.47: Fe-Cr-Ni pseudo binary diagram for general solidification mode of filler metals

The solidification mode of filler metal directly influences its cracking susceptibility (Figure 5.48). Austenite has the highest cracking susceptibility, whereas F-A mode is least susceptible to failure due to cracking. F mode of solidification also has substantially lower susceptibility and presents good resistance against cracking.

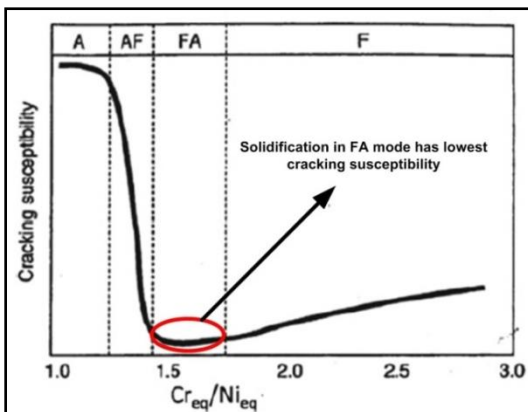


Figure 5.48: Cracking susceptibility for solidification mode of filler metals [Rathod et al., 2019]

The microstructure examination of weld fusion zone indicates that solidification of super duplex 2594 filler in the weld zone results in a mixed microstructure comprising of reformed austenite and ferrite phases. The cooling of the weld causes formation of reformed austenites due to ferrite transformation in the cooling process. Austenite present in the weld zone appears in various morphologies, each of which is precipitated in sequential order (Fig 5.49).

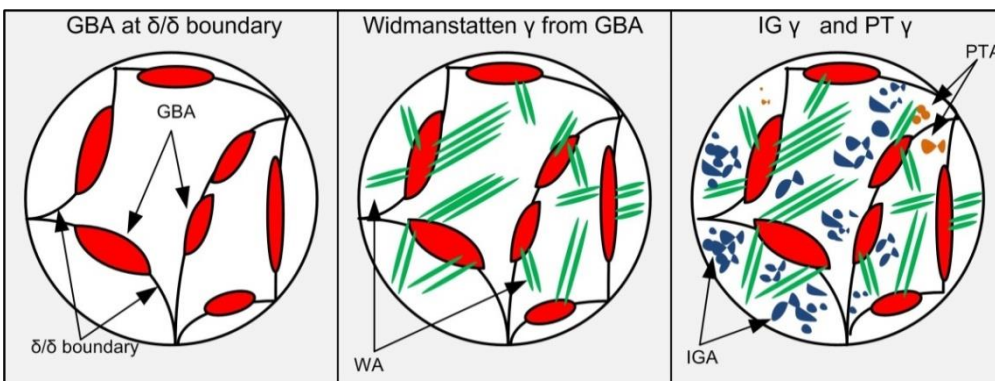


Figure 5.49: Precipitation of reformed austenites in super duplex filler weld

The first morphology of reformed austenite to develop is the grain boundary austenite (GBA), which happens at the already existing ferrite (δ/δ) boundary. The formation of GBA is favored at a high-temperature range; hence it marks its presence in the initial phase before significant cooling of the weld zone occurs. As the cooling continues further, wedge-shaped widmanstätten austenite (WA) nucleates. The nucleation of WA is initiated either at the ferrite (δ/δ) boundary or from partially transformed austenite (PTA) at the δ/γ boundary. Intergranular austenite (IGA) is the last to form, located within the ferrite matrix. The nucleation of IGA is favored at the lower temperature ranges; hence it precipitates when sufficient cooling of the weld has already happened [Hajiannia et al., 2013]. Filler wire 309L solidifies as primary delta ferrite (δ) and shows skeletal ferrite morphology perpendicular to the direction of the fusion line [Kellai et al., 2018]. Lippold and Kotecki have suggested that a low cooling rate of weldments and/or low C_{req}/N_{req} ratio favors skeletal ferrite morphology [Lippold et al., 2005]. The formation of skeletal ferrite is mainly due to the rejection of Cr from austenite and Ni from ferrite phases. The high nickel and less chromium, molybdenum content in the filler favors solidification in ferrite-austenite mode [Hajiannia et al., 2013]. The microstructure of 309L filler shows an interdendritic ferrite placed between the primary and secondary dendrite arms. This interdendritic microstructure of ferrite is known to be instrumental in preventing solidification and liquation cracking. They are also known to impart considerable impact toughness to the weld. The solidification in this weld progresses by a peritectic-eutectic reaction $L \rightarrow L + \delta \rightarrow L + \delta + \gamma \rightarrow \delta + \gamma$ where prior δ ferrite phase transforms to austenite. The transformed austenites are usually placed in the interdendritic region and between the ferrite cells. Comparing the weld zone microstructure, it was observed that in both the cases, region near the fusion boundary has a dominant presence of dendritic structures in the heat flow direction [Verma et al., 2016; Rahmani et al., 2018]. The super duplex filler 2594 has the precipitation of ferrite along with reformed austenites in multiple morphologies, whereas 309L solidifies with precipitation of only the skeletal ferrites in an austenite matrix. The dendrites near the fusion boundary are aligned almost perpendicular to it, whereas those in the center are aligned in multiple directions aligning with the heat transfer direction. The microstructure of weld fusion zone along with inverse pole figure maps (IPF) obtained from EBSD for both fillers made welds is presented below in Figure 5.50 and Figure 5.51. The microstructure in different sections of the weld is shown in Figure 5.52.

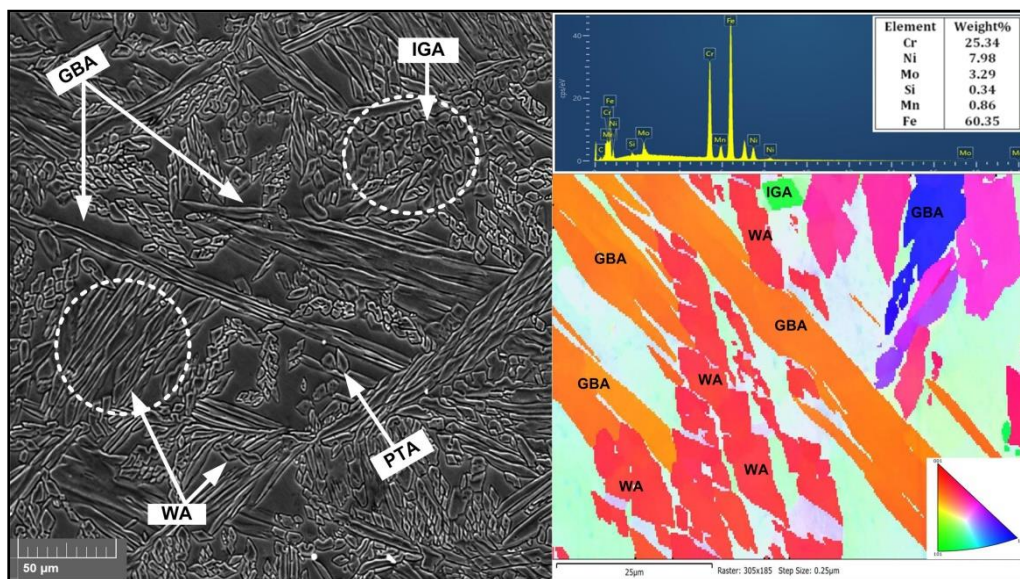


Figure 5.50: Microstructure of weld fusion zone for filler metal SDSS 2594

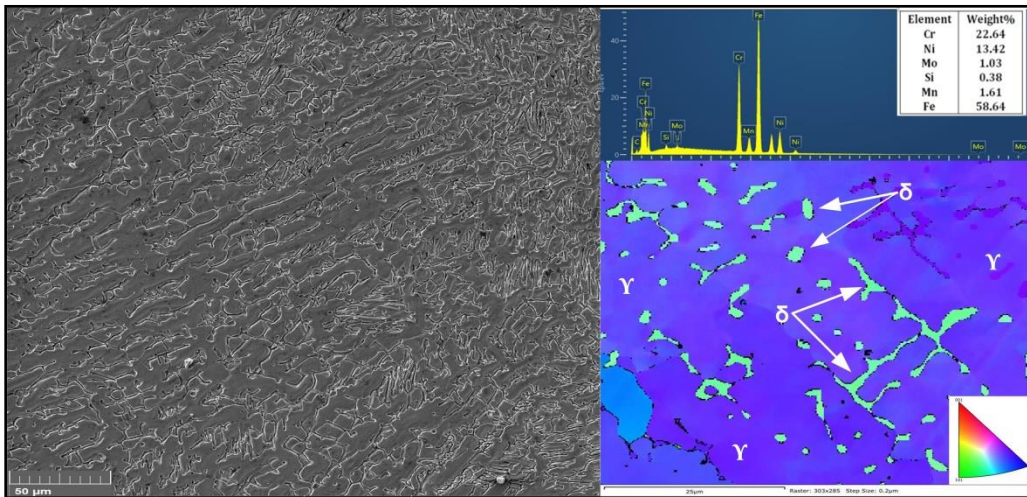


Figure 5.51: Microstructure of weld fusion zone for filler metal ASS 309L

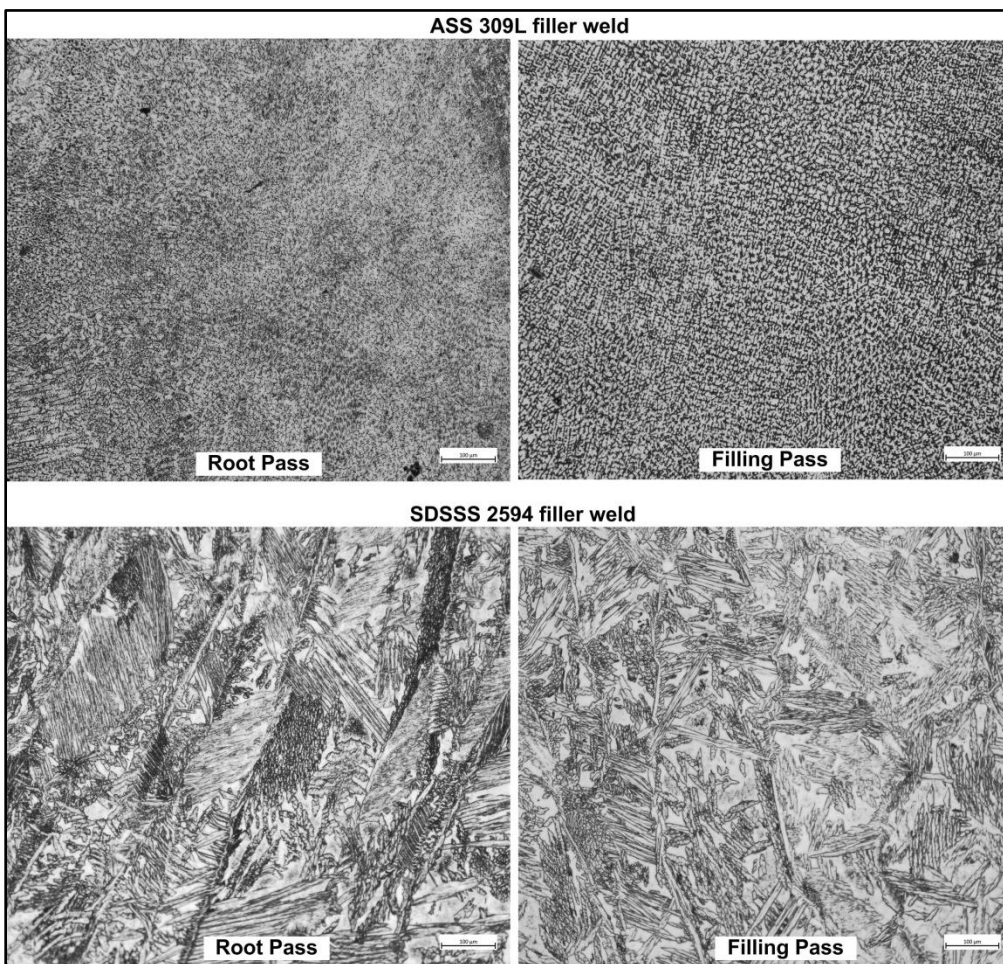


Figure 5.52: Microstructure in different sections of GTA weld

Rietveld refinement of weld zone XRD verifies the δ and γ phases in the weld fusion zone (Figure 5.53(a-b)). The δ/γ ratio was found to be 38/62 for weld made with super duplex 2594 filler and 11/89 for austenitic 309L filler.

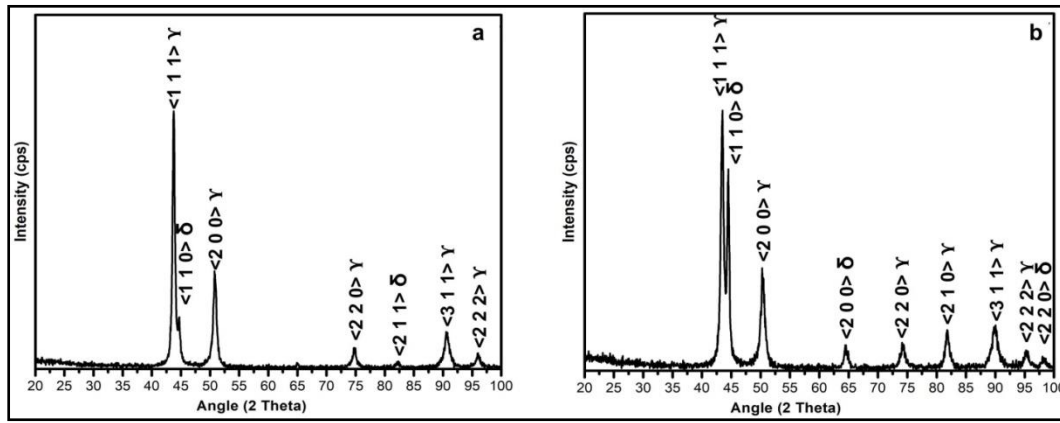


Figure 5.53: XRD of weld fusion zone for filler metals: (a) ASS 309L (b) SDSS 2594

The welds made with super duplex filler 2594 filler and austenitic 309L filler were found to have approximately 38.3% and 37.2% dilutions respectively. Based on dilution calculations, the fusion zone chemistry for weld made with super duplex 2594 filler metal was found to be composed of 21.62% Cr, 7.51% Ni, 3.17% Mo, 0.34% Si, and 0.74% Mn. Whereas, for weld made with austenitic 309L filler, the dilution based chemistry of weld fusion zone was found to be 21.2% Cr, 10.87% Ni, 0.67% Mo, 0.38% Si, and 1.6% Mn. Scheil solidification calculations have been used to predict the evolution of solid-phase fraction in the weld fusion zone. Scheil solidification also suggests that weld made with filler 2594 solidifies in a temperature drop of approximately 86.6°C, whereas weld made with filler 309L solidifies comparatively faster in about 52.2°C temperature drop. Moreover, the difference in equilibrium and non-equilibrium solidification temperature for weld made with 309L filler (29.2°C) is smaller than weld made with super duplex 2594 filler (61.1°C). The Scheil solidification curves for both the welds are presented in Figure 5.54(a-b), whereas the findings are summarized in Table 5.25.

Table 5.25: Transformation temperatures calculated using Thermo-calc

Transformation	Temperature (°C)	
	Weld 309L filler	Weld 2594 filler
Liquid starts to transform into primary δ	1442.9	1492.4
Start of the formation of γ	1424.9	1422.8
Solidification with $\delta + \gamma$ completes	1390.6	1405.7

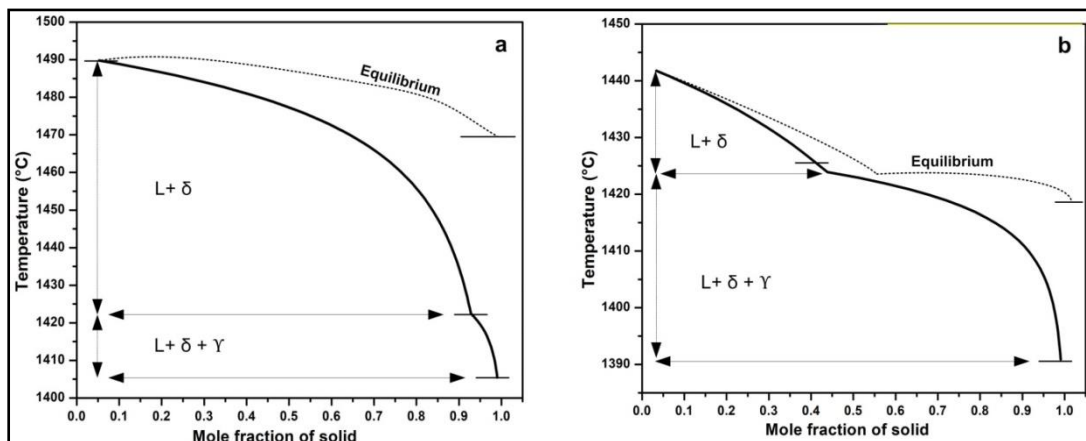


Figure 5.54: Calculations of Scheil solidification: (a) Weld by 2594 filler (b) Weld by 309L filler

ThermoCalc has also been used to calculate the mole fraction of different phases as a function of temperature (Figure 5.55 and Figure 5.56). The phase fraction diagram of 309L filler weld indicates that precipitation of δ -ferrite starts around 1441°C and dissolves around 967°C, later upon further cooling; low temperature α -ferrite again precipitates around 558°C. The austenite (γ) precipitation in the weld fusion zone starts around 1424°C. The results also indicate the

precipitation of the sigma (σ) phase around 974°C, whose dissolution occurs at around 393°C. Although the results from ThermoCalc suggest presence of very small proportion of secondary phases such as sigma and chi (<0.05 mol fraction), the final microstructure is devoid of any intermetallic /secondary phase and is constituted of δ and γ only. This suggestive precipitation of secondary phases is mainly due to Cr and Ni rich weld fusion zone chemistry, but all such deleterious phases dissolve upon weld cooling to the room temperature. In super duplex 2594 filler weld the solidification occurs in primary ferritic mode, and precipitation of ferrite begins around 1490°C, which continues till 940°C, and further again precipitation of α -ferrite occurs around 609°C, which remains in the final microstructure. As the cooling of weld occurs, austenite precipitation starts at around 1207°C. The diagram indicates that an intermetallic phase chi precipitates about 710°C, but it dissolves around 395°C. Similarly, sigma (σ) phase formation occurs around 1015°C. Although the diagram shows their presence in a minimal quantity in the weld pool at a temperature of around 250°C, the final solidified microstructure investigation reveals that weld is free from the σ phase, which indicates that weld cools too fast. The fast cooling of weld prevents the formation of any such phases in the final solidified microstructure.

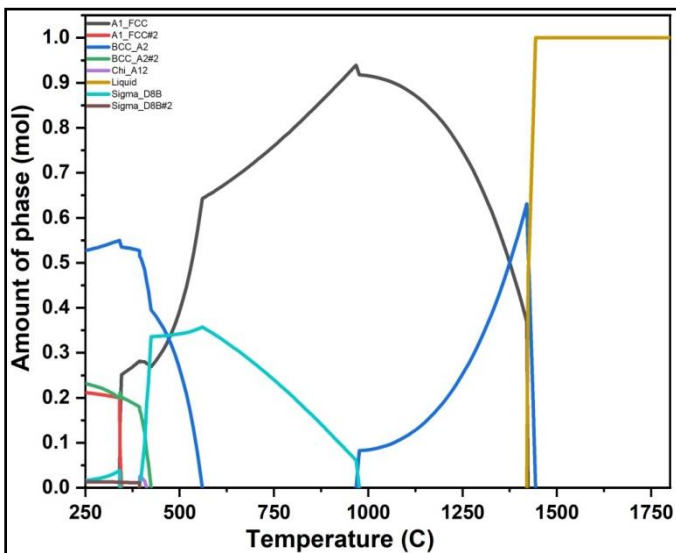


Figure 5.55: Equilibrium phase calculation for the 309L filler weld using ThermoCalc

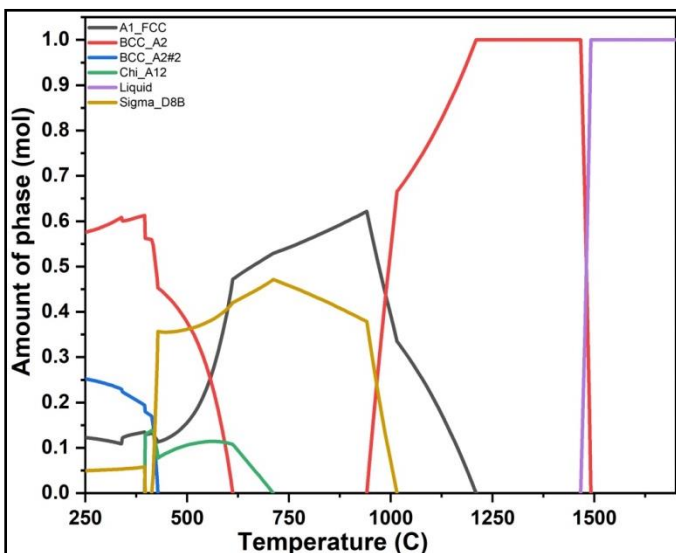


Figure 5.56: Equilibrium phase calculation for the 2594 filler weld using ThermoCalc

Microstructure of HAZ of X70 using 309L stainless steel and super duplex stainless steel filler mainly consists of bainitic ferrite with a mixture of carbides in the coarse prior austenite grains

(Figure 5.57). The bainite laths were limited to austenite grains as they form by displacive mechanism and cannot extend beyond austenite grains. X70 steel is a high-strength low alloyed steel alloyed with well-balanced microalloying additions (Nb, Ti, V), which forms carbides/carbonitrides. These precipitates will dissolve at higher temperatures ($>1200^{\circ}\text{C}$) and promote austenite grain size. In the CGHAZ, the peak temperatures are sufficient to dissolve these precipitates; therefore, the prior austenite grain size increased. Furthermore, a minor fraction of granular bainite with M/A constituents was also observed, which is a characteristic of continuous cooling in the heat-affected zone. Microstructure investigation of HAZ on API X70 side also shows the formation of the type II boundary for both the fillers. This boundary runs parallel to the fusion boundary and is at a distance of a few μm from it. Non-homogeneity between base and filler metal leads to the development of an unmixed region distinguished by a type II boundary, which is formed during the cooling of molten filler. The crystal structure of X70 and filler austenitic 309L, super duplex 2594, are different, which causes improper wetting of substrate along the fusion zone. The non-zero contact angle and corresponding free energy pose a challenge to the growth of solid at the fusion boundary suppressing the normal epitaxial growth. This type II boundary often becomes a favorable site for precipitation of carbon in case of a significant magnitude of migration occurring from base metal.

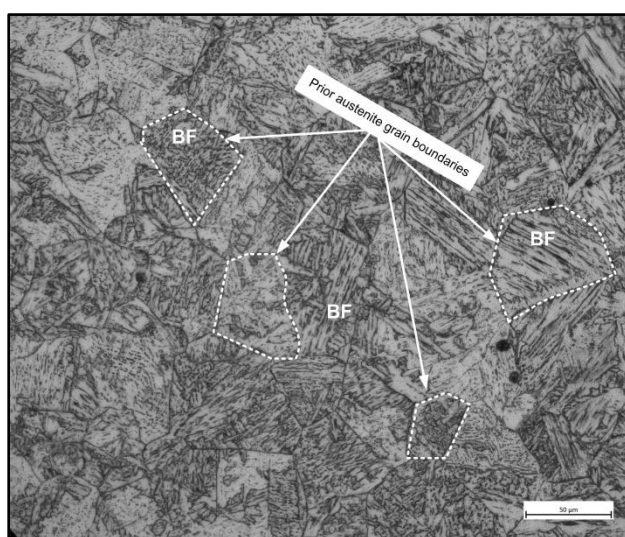


Figure 5.57: Heat affected zone on X70 side for super duplex filler [BF: Bainitic Ferrite]

The heat affected zone on the super duplex side consists of a ferrite matrix containing a network of austenite grains. In a multi-pass weld, the heat-affected zone is exposed to a thermal cycle where after heating to a very high temperature, the weld is held for a short time interval and then cooled to room temperature. Due to this cycling, except the partially transformed austenite, all other austenite transforms to ferrite. The heat-affected zone on the super duplex side is also very narrow. Repeated thermal cycle and higher cooling rate suppress the formation of reformed austenite as compared to the weld zone. In multi-pass welding, due to the reheating of the heat-affected zone, secondary austenite precipitation occurs. The microstructure of heat affected zone on the super duplex side undergoes a sequential process of austenite-ferrite transformation, grain growth, and coarsening during heating and ferrite-austenite transformation during cooling (Figure 5.58).

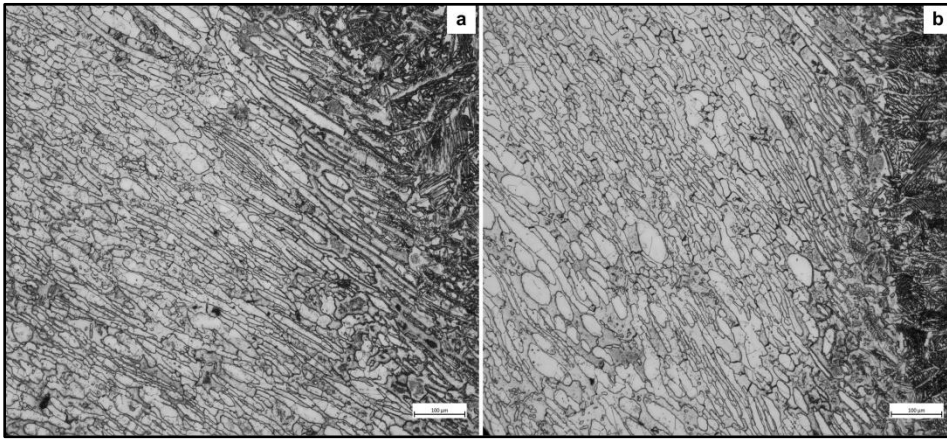


Fig 5.58: HAZ on super duplex side for welds with: (a) super duplex 2594 filler metal (b) austenitic 309L filler metal

The microstructure evolution in the weld and transition zone of weldments was also confirmed using the Schaeffler diagram (Fig 5.59).

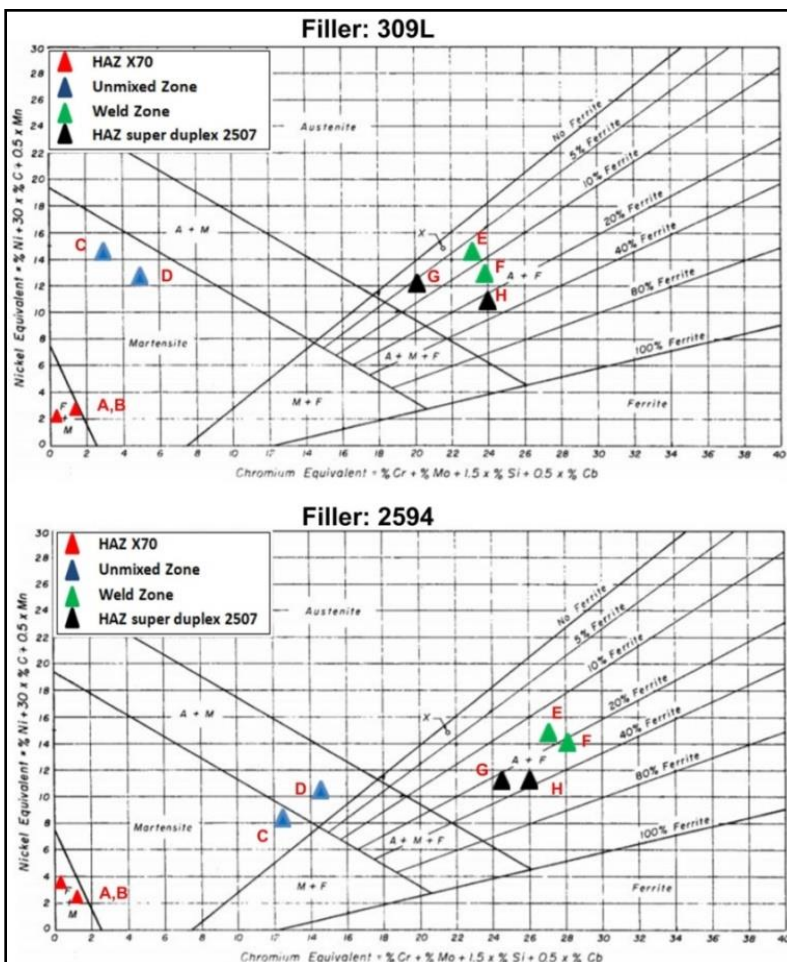


Figure 5.59: Schaeffler diagram for predicting microstructure [Guiraldenq et al., 2017]

Ferrite fraction is an important microstructure variable, which influences weld characteristics [Hosseini et al., 2019]. Ferrite content of weld is significantly influenced by the chemical composition and thermal exposure in the multi-pass process, which in turn affects toughness, corrosion, and hot cracking resistance [Taban et al., 2014]. Ferrite number gives a fair estimation of weld's ferrite content, and it can be theoretically calculated using Schaeffler and WRC-1992 diagram. Figure 5.60 below represents Schaeffler and WRC-1992 diagram for the weld. WRC-1992 diagram is more suitable for nitrogen-containing fillers, such as super duplex 2594, as it

contains an extra term accommodating nitrogen, whereas Schaeffler lacks the same [Kotecki et al., 1992]. Nitrogen is a strong inhibitor of pitting corrosion and as well as austenite promoter; hence it being taken into consideration is very important. The solidification is primarily in the fully ferritic mode, from which austenite precipitates as the cooling happens. The formation of austenite starts at grain boundaries and further proceeds to intergranular directions. This transformation resulting in ferrite-austenite microstructure depends on ferrite solvus temperature, which separates single phase ferrite fields from the dual-phase ferrite field [Hajiannia et al., 2013]. The WRC-1992 diagram indicates ferrite content in the range of approximately 50% and solidification in ferritic mode, whereas the Schaeffler diagram predicts the solidification in ferrite-austenite mode with ferrite content around 30%.

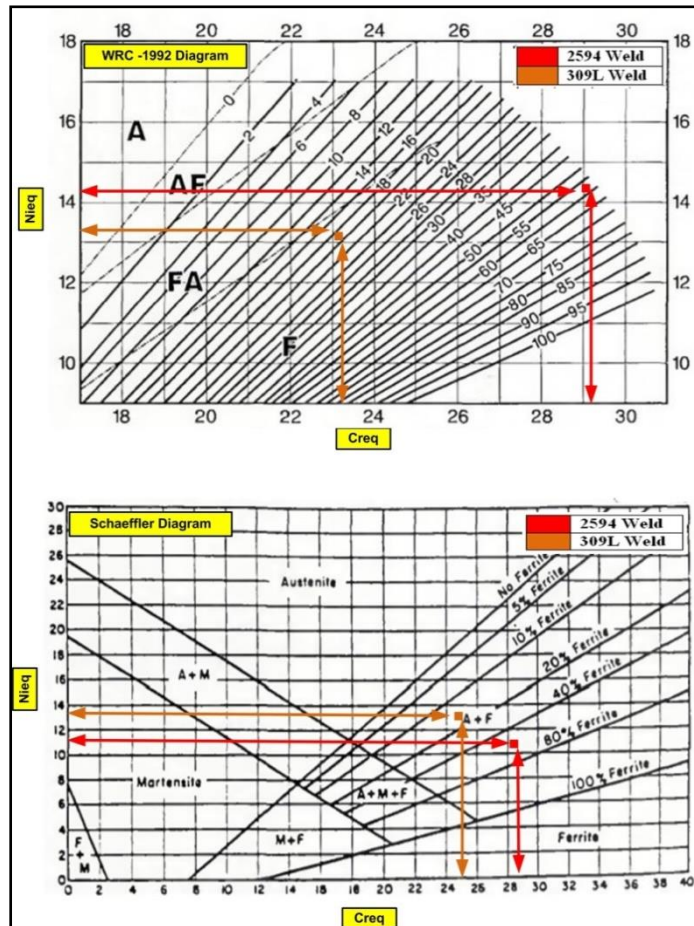


Figure 5.60: WRC-1992 and Schaeffler diagram for weld [Kotecki et al., 1992]

5.6.3. MECHANICAL CHARACTERIZATION OF GTA WELDS

The ultimate tensile strength of both the welds was superior to ferritic X70 steel in the as-received condition. The difference in chemical composition and solidification microstructure causes weld with filler 2594 to have a superior tensile strength of 803 MPa with its mismatch with X70 and SDSS 2507 being 1.33 and 0.97 respectively. The weld fabricated with 309L filler has strength of 676 MPa and mismatch of 1.12 and 0.82 with API X70 and SDSS 2507 respectively. During the transverse sample testing, both the weldments failed at the weaker parent metal X70 side, away from the weld zone. The corresponding tensile test results are summarized in Table 5.26. Fractography of weld specimens at high magnifications using scanning electron microscopy is shown in Figure 5.61. The absence of a perfectly matching surface rules out the possibility of cleavage fracture being the primary mode. A low percentage of cleavage facets on the fracture surface also support this observation. The fractured surface in both the welds comprises dimples, ductile dimples, cleavage facets, and tear ridges. This shows

that the failure of weld has occurred in a mixed-mode. The broken tensile specimen of 309L filler weld has a more dominant cup and cone structure. Transgranular ductile dimples dominate the fractured surface of both welds. Dimples are present in a major fraction, which is comparatively more in 2594 filler weld. Multipass welding leads to the tempering of the weld zone, which causes grain coarsening and micro void occurrence. The coalescence of these microvoids further leads to ductile tearing and makes the welds ductile. Reformed austenite formed in the weld zone of 2594 filler is mainly due to tempering and repetitive heating and cooling in the multi-pass weld. Hence, it is more prone to develop micro voids and favor the ductile tearing mode of failure. The elongation in 309L weld is also almost in the range of 2594 filler weld, which indicates that even interdendritic ferrites favor the ductile tearing mode. The presence of a small proportion of tearing ridges signifies that tearing of weld might have occurred in the very initial stage, where it could have been an initiating factor of failure. But as the tensile load increases, the ductile tearing would have dominated the failure mode.

Table 5.26: Tensile Properties of GTA welds and base metals

Specimen	Ultimate Tensile Strength (MPa)	Mismatch with X70	Mismatch with SDSS	Elongation (%)
X70	602.1 ± 15	-	-	20.1
SDSS 2507	820.6 ± 12	-	-	40.4
Weld with Filler 309L	676.3 ± 20	1.12	0.82	30.5
Weld with filler 2594	803.1 ± 18	1.33	0.97	33.8

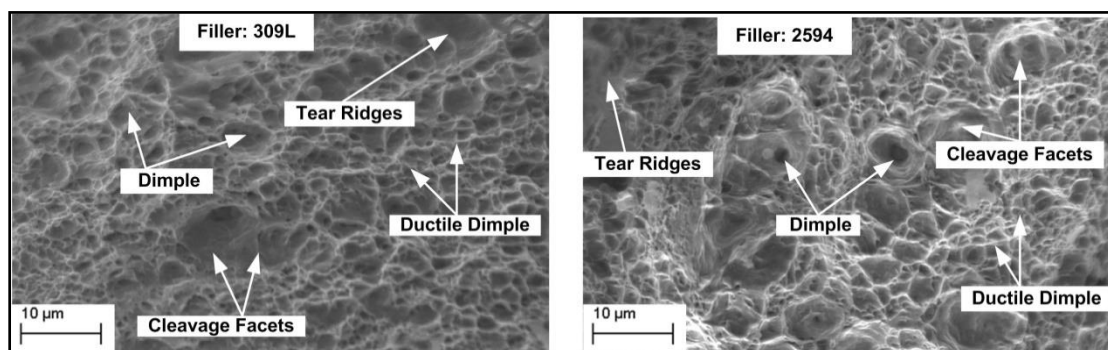


Fig 5.61: Fractograph of tensile specimen

The filler 309L has superior impact strength as compared to the filler 2594. The skeletal microstructure of ferrite in 309L is known to lower the chances of solidification and liquation cracking along with imparting considerable impact strength to the weld. The weld with austenitic filler showed an approximate enhancement of 11% impact energy in the weld zone. The specimen with a notch in the HAZ region of the X70 side shows the inferior impact energy in both the cases and is hence most prone to failure location. The HAZ on the super duplex side has an almost similar elemental composition as that of the weld. Moreover, the microstructure phases are also similar to changes occurring due to tempering owing to the heating and cooling cycle in multi-pass welding. Hence the impact energy of specimens with a notch in HAZ of the super duplex side is inferior but remains in range with that of the weld zone.

Table 5.27: Impact Energy of base and weld specimen

Zone	Region/Zone	Impact Energy (J)
Weld 309L filler	Weld zone	162 ± 6
	HAZ X70	105 ± 4
	HAZ 2507	145 ± 7
Weld 2594 filler	Weld zone	145 ± 8
	HAZ X70	98 ± 3
	HAZ 2507	128 ± 4

The microhardness profile is similar in trend for both the fillers (Figure 5.62). A sharp contrast in values is observed in different transition zones of the weld. The difference in chemical composition, morphology, and microstructure distribution leads to variation in hardness. The hardness of the weld zone in filler 2594 is comparatively higher as compared to 309L. A sudden increase in the HAZ region microhardness on the X70 side is due to the formation of an unmixed zone, migration of alloying elements from the weld, and carbon from the X70 base side. Super duplex side heat-affected zone for SDSS 2594 filler remains in the same range as that with the base metal, due to comparable chemical composition and microstructure. This variation in hardness does not deteriorate the overall weld performance because the high hardness transition zone's width is very small. Hence, the overall structural integrity of weld remains intact.

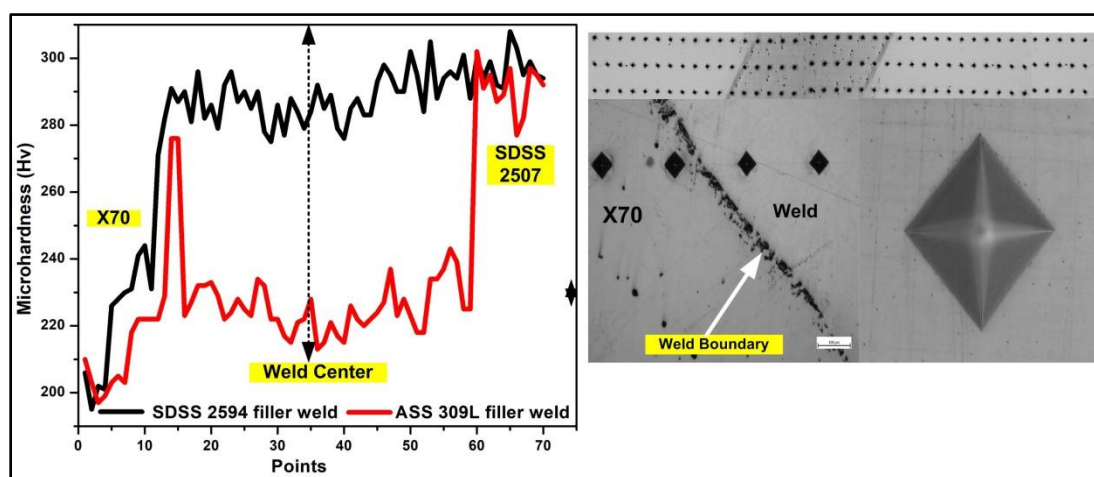


Fig 5.62: Microhardness profile of welds

5.6.4. CHARACTERIZATION OF WELDS FOR CORROSION RESISTANCE

A potentiostat with three-electrode cells was used to measure the specimen's corrosion characteristic in the 3.5% NaCl solution environment at a scan rate of 0.167 mV/s in the potential range of -0.25 mV +0.25 mV against the open circuit potential. Open circuit potential was obtained by leaving the specimen in the electrolytic solution for 600 seconds. The potentiostat uses an Ag/AgCl electrode, graphite rod, and specimen under investigation as the reference, counter, and work electrode, respectively. The investigated specimens were drawn from the base metal, weld fusion zone, and heat affected zone on both sides of the weld (Figure 5.63). Before exposing to the aqueous environment, the test specimen was polished by successively grinding against the SiC papers from grit size 80 to 600. The polished surface was cleaned with acetone to remove any contamination and impurities from the exposed surface.

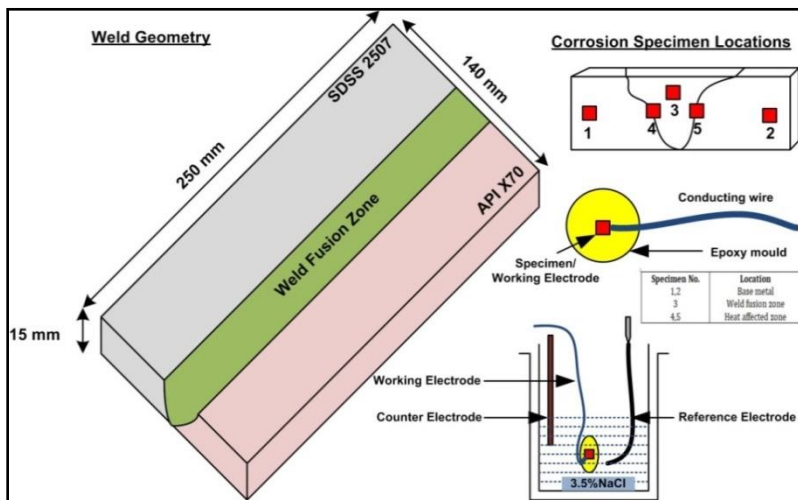


Fig 5.63: Schematic of corrosion investigation

The corrosion measurement reveals a significant difference in the corrosion resistance of the two base metals (Figure 5.64a). The corrosion potential (E_{corr}) of API X70 pipeline steel (-382.7 mV) was low compared to the super duplex stainless steel 2507 (-211.1 mV), which is one of the major reasons for joining the latter material with former in the critical locations. The corrosion potential of the 309L filler weld (-114.1 mV) was found to be superior to the super duplex 2594 filler weld (-242.3 mV) (Figure 5.64b). Tafel plots for different zones of weldments (base metals, weld fusion zone, and heat affected zone) are shown in Figure 5.64(a-d) and the results are summarized in Table 5.28.

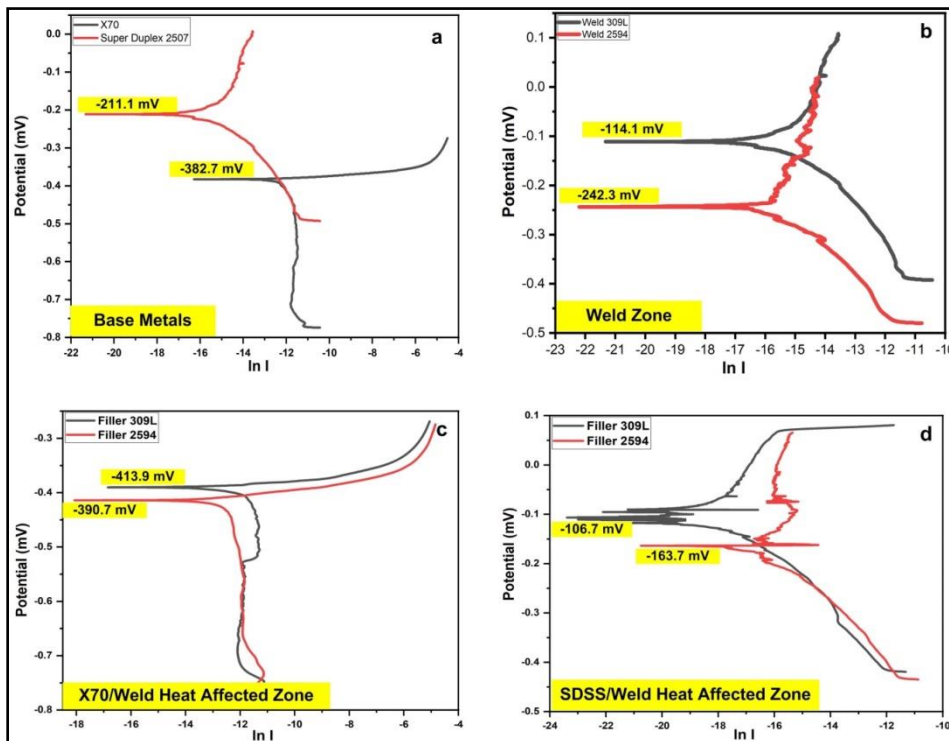


Figure 5.64: Tafel plot for different zones of dissimilar welds: (a) Base metals (b) Weld zone (c) HAZ on X70 side (d) HAZ on SDSS side

Table 5.28: Corrosion potential of base metals and welds

Specimen	Corrosion Potential E_{corr} (mV)
API X70 pipeline steel	-382.7
Super Duplex 2507 steel	-211.1
E309L filler weld fusion zone	-114.1

SDSS 2594 filler weld fusion zone	-242.3
E309L filler X70 heat affected zone	-390.7
SDSS 2594 filler X70 heat affected zone	-413.9
E309L filler SDSS2507 heat affected zone	-106.7
SDSS 2594 filler SDSS2507 heat affected zone	-163.7

EBSD investigation indicates that 2594 filler weld has more high angle grain boundaries ($>15^\circ$) and Kernel Average Misorientation (KAM) as compared to 309L filler weld (Figure 5.65). Super duplex 2594 filler weld has 63.1% high angle grain boundaries (HAGBs), whereas in 309L filler weld, the HAGBs is 32.6%. High-angle grain boundaries are more reactive to the electrolytic solution; hence, their higher proportion accelerates the corrosion. The Kernel Average Misorientation (KAM) measures the average misorientation angle of a point with its neighbors. Misorientation is known to generate 'hotspots' sites with a significant angular difference with adjacent grains. This misorientation of grains provides a reactive environment favorable to the aqueous solution, thereby increasing the susceptibility of the specimen to corrosion. The maximum degree of Kernel Average Misorientation (KAM) for the 309L filler weld (4.97°) is higher compared to the super duplex 2594 filler weld (2.75°). Still, the wider spread of misorientation in the latter makes it more susceptible to corrosion. The number of hotspots in 2594 filler weld is also higher as compared to 309L filler weld. Increased spread of hotspots indicates there are more sites with angular misorientation between the grain boundaries. Grain size can also be used as a sensitive indicator of corrosion performance along with other parameters discussed above. The super duplex filler weld has grains of various diameters (μm) across the fusion zone. The maximum fraction of grains (17%) lies in the approximate range of 80 μm diameter followed by 12% for approximately 55 μm and 35 μm diameters. The precipitation of austenite in various morphologies upon cooling of the weld makes the microstructure a combination of different grains sizes. The low diameters can be attributed to the partially transformed and intergranular austenites, whereas the higher grain diameters correspond to widmanstatten and grain boundary austenites. In the case of 309L filler weld, γ matrix has around 87% grains in the range of 85 μm diameter along with δ in skeletal morphology having the minor presence of 2-4% in the average diameter ranges of 2.5 μm , 5 μm , 15 μm , and 22.5 μm (Figure 5.66). The lesser variation in grain sizes offers more uniform grains, hence providing a less reactive environment for corrosion to act on the grain boundaries.

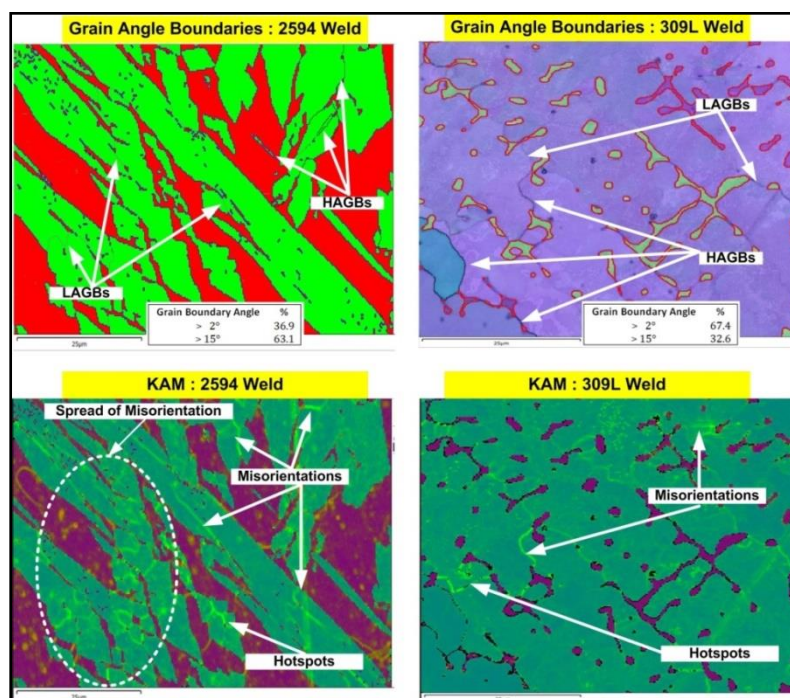


Figure 5.65: Grain boundary angle and KAM in weld fusion zones

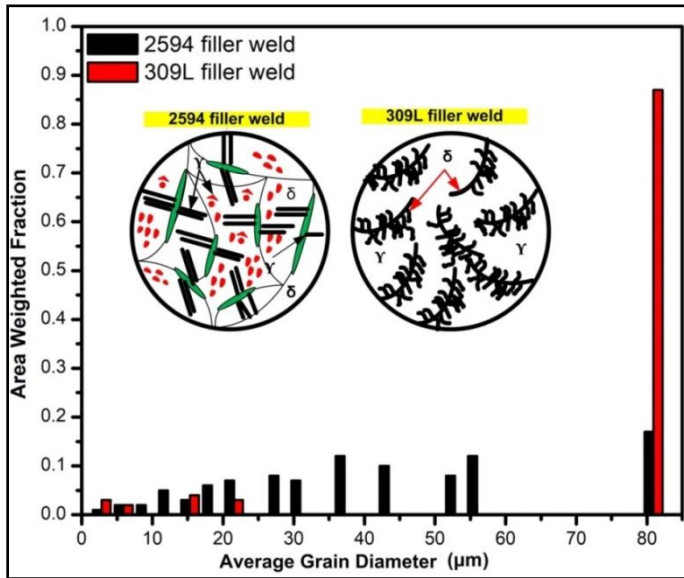


Figure 5.66: Distribution of average diameters of δ and γ grains in the weld zones

The corrosion investigations reveal that the heat affected zone on the X70 side is the most prone region for corrosion. This region shows a corrosion potential comparable to X70 steel and much lower than the weld fusion zone. The corrosion potential of the heat affected zone on the X70 side is almost similar for both the filler welds. Due to the inclusion of weld area in heat affected zone specimen, the 309L heat affected zone specimen has marginally higher E_{corr} (-390.7 mV) as compared to 2594 filler weld (-413.9 mV). As discussed above, the corrosion resistance of super duplex filler weld is inferior to austenitic 309L; its inclusion in heat affected zone specimen contributes to the lower corrosion resistance. EBSD analysis of heat affected zone on X70 side reveals precipitation of certain un-indexed phases, possibly linked with the existence of M/A constituents and grain boundaries in the proximity of fusion line (Figure 5.67). The distribution of M/A at grain boundaries makes its separation and quantification difficult. M/A constituents can have a significant influence on properties of HAZ [Huda, 2019b; Huda et al., (2019c)]. The proportion of HAGBs in the heat affected zone of super duplex 2594 and austenitic 309L filler is 65.7% and 61.9%. There is slight precipitation of Cr_7C_3 in the unmixed zone, for both welds, which can be attributed to the high gradient of chromium concentration in X70 and weld zone, which leads to a significant carbon migration across the boundary and formation of carbides in the unmixed zone. The presence of Cr_7C_3 in a small proportion (0.3% and 0.2%) makes its detection and distinction difficult by microscopy techniques. The elemental composition quantified using EPMA, and corresponding element maps obtained using EDS at the X70/weld interface is represented in Figure 5.68. The elemental composition readings were taken at a successive interval of 20 μm in the region away from weld boundary, whereas for the region in proximity of fusion line, the successive distance was reduced to 3 μm . The measurement taken over a length of approximately 1000 μm , covers the heat affected zone, unmixed zone, and weld fusion zone. The elemental composition plots of both the filler welds suggest almost negligible presence of Cr, Ni and Mo in the HAZ region of pipeline steel. These elemental compositions witness a sharp increase in the region of unmixed/partially melted zone, which can further increase as the location crossing the fusion line and reaching weld fusion zone. This sharp gradient in elemental composition of Cr can lead to significant carbon activity in this region.

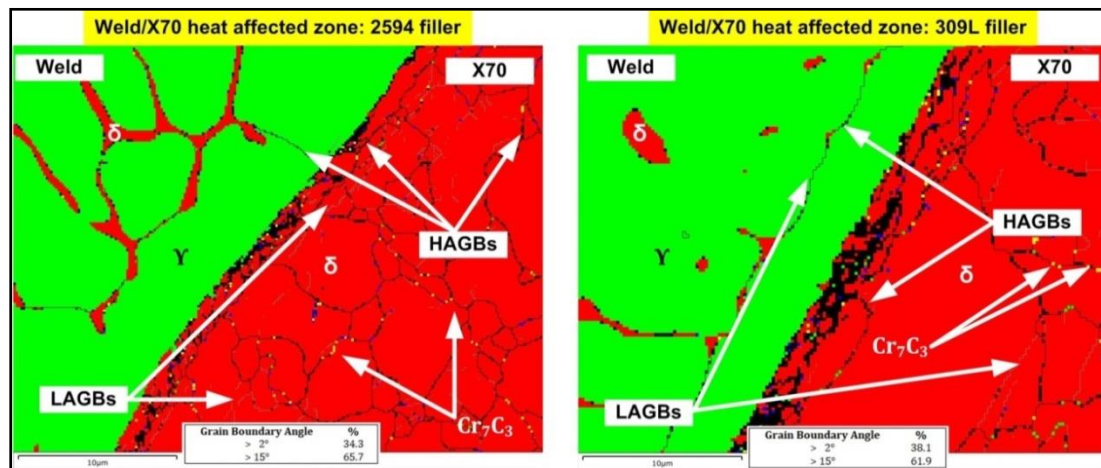


Figure 5.67: Grain boundary angle in heat affected zone

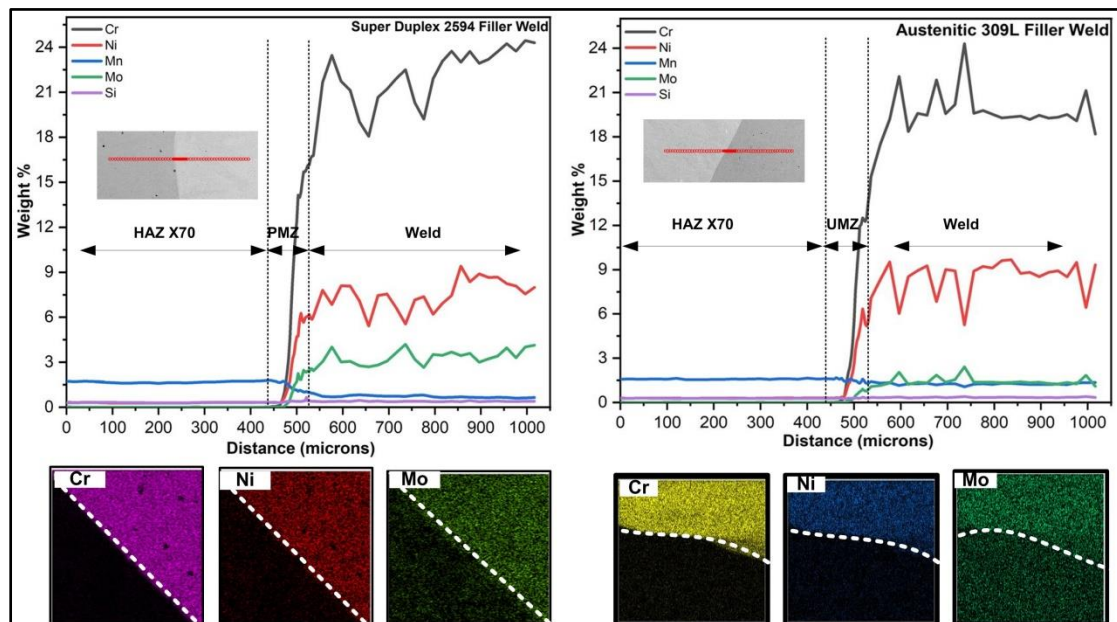


Figure 5.68: Elemental analysis at X70/Weld interphase

High angle grain boundaries and significant differences in Cr, Ni concentration in γ/δ phases makes the grain boundary the most susceptible region for the initiation of pitting. But as the electrochemical reactions proceed, the pits mature, and they collectively appear to locate on the grain boundaries and intergranular region. The hydrolysis of pits leads to its propagation on all sides and covers multiple grains, appearing as a lacy cover on the surface. The scanning electron microscopy images of corroded specimens reveal the pitting to be severely harsh and covering a much larger area. The pitting in the heat affected zone appears to initiate at a few micrometer distance away from the weld fusion line. The region in the unmixed zone also shows pitting, but the pits are small and discontinuous. Figure 5.69 shows images of pitting observed in this study. Both the filler metals belong to the family of stainless steel and hence are corrosion resistant as the base metal super duplex stainless steel. The homogeneity in chemical composition results in heat affected zone specimen on the super duplex side having highest corrosion potential amongst all zones.

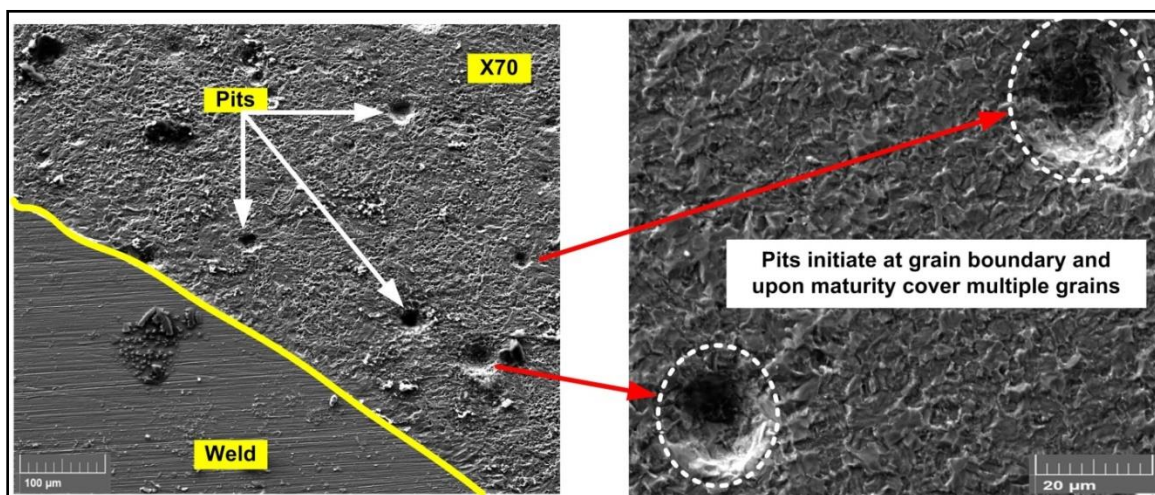


Figure 5.69: Pitting in heat affected zone on X70 side

5.7. EFFECT OF HEAT TREATMENT ON WEAR & CORROSION BEHAVIOR OF SUPER DUPLEX STAINLESS STEEL 2507

5.7.1. WEAR BEHAVIOR INVESTIGATIONS OF SUPER DUPLEX STAINLESS STEEL 2507

Super duplex stainless steel when subjected to different manufacturing process such as welding, hot forming may be exposed to high-temperature ranges for a long time which leads to the precipitation of the above mentioned intermetallic/secondary phases. These are deleterious phases which decrease Cr and Ni content, hence lowers the PRE_N and has a negative impact on characteristic properties [Pardal et al., 2010]. A number of researchers have investigated the effect of sigma phase, formation kinetics, and effect on mechanical properties including wear [Lu et al., 2001; Fargas et al., 2013; Fonseca et al., 2017]. Limited literature is available about the other secondary phases and its impact on properties [Pohl et al., 2007; Escriba et al., 2009; Isern et al., 2016]. None of the studies have yet taken into consideration all the possible secondary phases that can develop owing to exposure to varied temperature ranges during manufacturing processes. The present work focusses upon the precipitation of several intermetallic/secondary phases in a super duplex stainless steel by giving suitable heat treatments and to study its effect on the wear behavior in the dry and wet condition comparable to the actual service environment. An attempt has also been made to realize the difference in the effect of chloride on wear behavior in the neutral and acidic medium. Progressive wear mechanism has also been analyzed using the geometrical change in pin's contact face profile and the corresponding wear and weight loss data obtained in experimentation. The wear mechanism has been estimated using scanning electron microscopy of the pin's worn surface. Heat treatment conditions (Table 5.29) were selected based on the Time-Temperature-Transformation diagram shown in Figure 5.70.

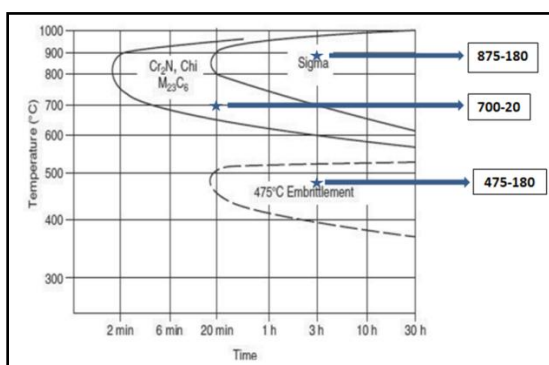


Figure 5.70: TTT diagram of a duplex stainless steel [Rosso et al., 2013]

Table 5.29: Heat Treatment Conditions

Temperature (°C)	Time (min)	Designation
475	180	475-180
700	20	700-20
875	180	875-180

The pins were made to slide over the disc made up of EN31 steel. EN31 has a hardness value greater than as compared to that of the super duplex 2507 steel. Wear test was carried out in dry and wet condition for sliding distances of 1000, 1500, 2000, 2500, 3000 m. To achieve the different sliding distances, the location of pin was changed with its distance from center being 21.2, 31.8, 41.2, 53, 63.6 mm respectively. Each test was repeatedly performed for three times with three different pin specimens and this section reports the mean value for each experimental data. The load for each sliding wear run was kept constant at 5N. Before and after each test pin was rubbed on an emery paper of grade 400 and then cleaned with acetone so as to ensure that there is no other particle sticking to the surface and proper contact between the pin and the disc surface is achieved. Pins were weighed before and after each test run on an electronic balance with a resolution of ± 0.1 mg. Weight loss method was used to determine wear volume and wear rate by applying Archard equation. The wear test was carried out in dry and wet condition. The wet condition includes the environment of 3.5% NaCl, 1 M HCl, 10^{-2} M sodium thiosulfate solution and artificial ocean water. Artificial ocean water has been prepared following ASTM standard D1141-98 [ASTM: D114198]. 3.5% NaCl and 1M HCl were selected in order to evaluate the effect of chloride in neutral and acidic media. Sodium Thiosulfate solution upon interaction with metal surface releases H_2S gas. Transportation in oil and gas industry refers to the movement of crude oil from the oil fields to refinery and further to the storage areas. In raw stage crude oil is transported either by tankers or by pipelines. The concentration of the H_2S in vapor phase above crude oil is found to be higher than the expected level. H_2S is highly corrosive and can severely deteriorate the properties of tanker and pipeline material. Super duplex stainless steel is one of the most suitable candidates which are employed for dissimilar joining in the pipeline industry [Mendoza et al., 2010; Bensaid et al., 2014]. Hence it is important to study the wear behavior of super duplex stainless steel in sodium thiosulfate environment owing to different intermetallic/secondary phases formed due to exposure to manufacturing processes in real time working condition. Carbon steel specimen exposed to $S_2O_3^{2-}$ containing solution develops a film on their surface which is mainly composed of iron sulfide and cementite. This film has a characteristic of good electron conductivity and non-passivation. The film controls the rate of H_2 absorption of steels exposed to thiosulfate solution, thus the surface concentration of H_2S increases as the concentration of $S_2O_3^{2-}$ increases [Kappes et al., 2011]. To simulate this condition the specimens were tested in the environment of sodium thiosulphate solution. Increasing application of super duplex stainless steel in offshore high risers makes it important to study the wear behavior and estimation of wear parameters in artificial ocean water. The pin's wear surface changes rapidly over the changing sliding distance. The change in shape and size of wear face in terms of wear track profile was studied by taking images on a stereomicroscope. Hardness has a direct relationship to the material's wear resistance. As received and heat treated specimen was tested for microhardness using a 150g load. Different phases formed due to applied heat treatments cause variation in the hardness. Precipitation of sigma phase in the specimen with condition 875-180 exhibits the maximum hardness (382 Hv) followed by the 475-180 (318 Hv) owing to the precipitation of α' . Chi phase precipitation increases the hardness of 700-20 (266 Hv) specimen marginally as compared to the as received specimen (243 Hv) which has the lowest hardness value.

Pin on disc wear testing method is employed at the lab level to estimate the material's wear behavior. The wear test results are usually analyzed using Archard's equation. Bressan et al. in their work have presented a detailed explanation for wear test methodology and calculations as per the Archard's equation [Bressan et al., 2008]. This equation establishes a co-relation between

different parameters of wear test. Mathematically Archard's equations can be used to derive several wear performance parameters as given in equations 5.4-5.7.

$$Q \text{ (mm}^3\text{/m)} = V / S = K F_N / H \quad (5.4)$$

$$K = QH / F_N = K_S H \quad (5.5)$$

$$K_S = Q / F_N \quad (5.6)$$

$$V = \Delta m / \rho \quad (5.7)$$

Where Q is the wear rate, V is the volume of material lost due to wear, S is the sliding distance in meter, F_N is the applied normal load and H is the hardness of softer material out of pin and disc. K is the wear coefficient which is most important and acceptable parameter for wear behavior comparison, and K_S is the specific wear coefficient. V i.e. the cumulative lost volume in mm^3 which appears in equation 1 is the most basic parameter and is calculated at lab level using the loss in weight of the sliding pin, Δm is the change in weight of the pin in g and ρ is the density of material in kg/m^3 . Comparative plot of wear property characteristics for dry sliding wear (Figure 5.71(a-c)) indicates specimen 875-180 and AR have the minimum and maximum wear rate. Specimen 700-20 and 475-180 lies in the intermediate region with their wear rates too inversely proportional to the hardness induced owing to phases formed because of heat treatment. A similar effect of precipitated phases can also be observed from Figure 5.72 where the wear in microns with respect to time confirms to the finding that the rate of wear in super duplex stainless steel 2507 follows the pattern: $AR > 700-20 > 475-180 > 875-180$.

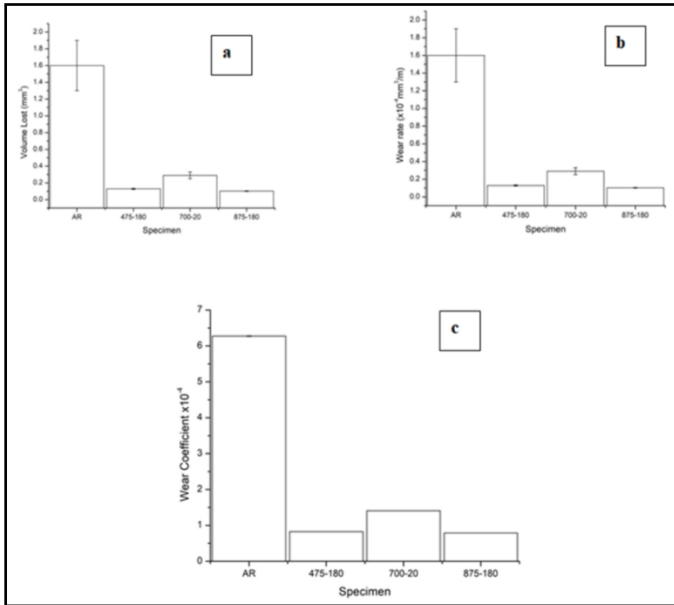


Figure 5.71: Wear property characteristics in dry sliding wear

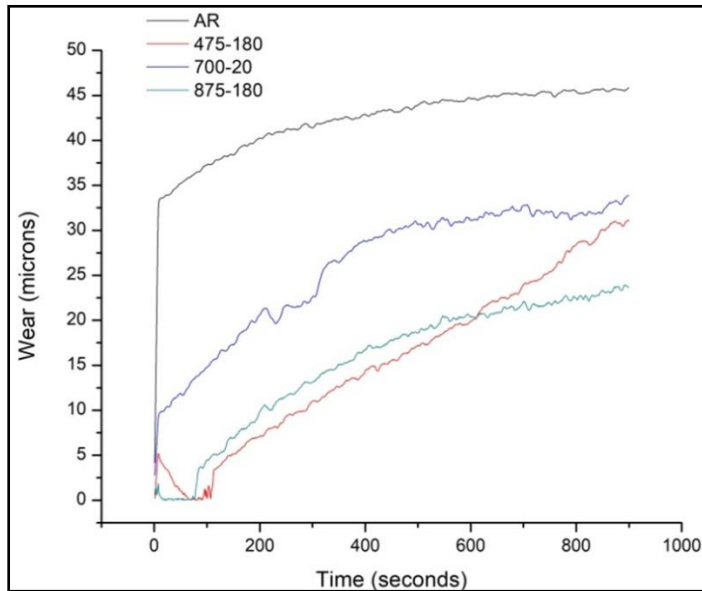


Figure 5.72: Wear with time in dry sliding wear test

The wet wear test in earlier-mentioned environments is an attempt to create an actual service working environment which may be very harsh and highly corrosive. Also, the fluid flushes out the metal debris or any other unwanted foreign particle that may stick to the face of the pin and can act as a hindrance between pin-disc contact interfaces. Results obtained from the pin on disc wear test shows that the trend of wear behavior remains the same as that in the dry condition (Figure 5.73 (a-c)).

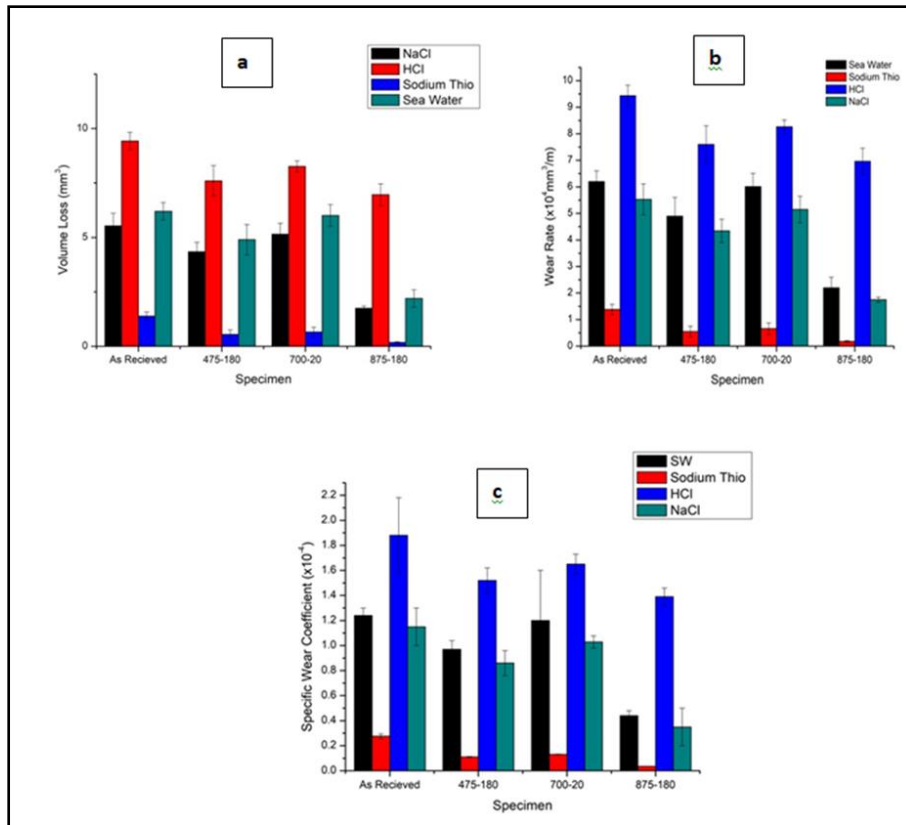


Figure 5.73: Comparison of wear parameters (a) Volume Loss (b) Wear Rate (c) Specific Wear Coefficient

The results obtained also provide us a comparison of wear behavior due to the action of chloride in the neutral and acidic medium. The specimen shows a significantly higher wear rate in HCl environment as compared to the NaCl solution. The reason behind this trend in the result is

directly related to the different chemical reactions occurring in both the mediums. In HCl solution, the cathodic reaction that is taking place is: $[2\text{H}^+ + 2\text{e}^- = \text{H}_2]$. This reaction leads to evolving of hydrogen. The evolved hydrogen from the medium gives way for more reaction to occur and hence consumes more electrons. In a NaCl solution, reduction of hydrogen in cathodic reaction takes place and it leads to the formation of the hydroxide group. The cathodic reaction in NaCl solution is: $[2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-]$. These hydroxides are absorbed on the surface of the metal and they, in turn, lower down the reaction kinetics. Increased rate of reaction due to the evolution of hydrogen in acidic medium induces weight loss, surface damage due to corrosion and hence increases the wear rate. This trend obtained in experimentation is shown in Figure 5.74.

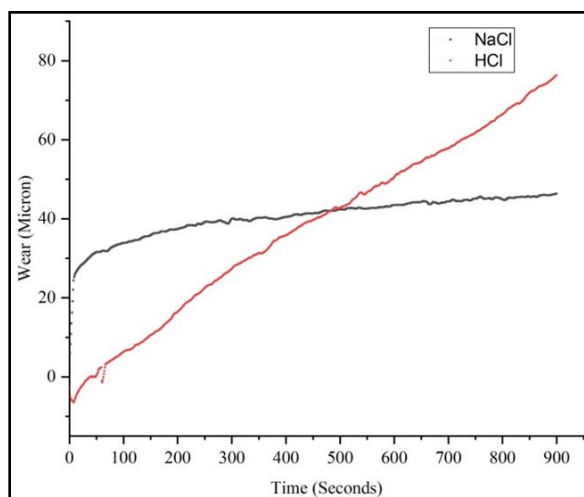


Figure 5.74: Comparison of Wear in NaCl and HCl medium

Super duplex stainless steel 2507 is now being used in the transportation of oil and gas where it is regarded as the most suitable candidate for obtaining dissimilar joint with API grade pipeline steel. Crude oil during transportation through the pipeline has H_2S gas over it in the vapor phase. Thus to study the effect of H_2S on wear behavior of super duplex stainless steel, the wet wear test was conducted in the environment of sodium thiosulfate solution. Super duplex steel 2507 due to its excellent corrosion properties are also ideal for marine application. The risers of oil drilling units and underwater drilling units are now being made of super duplex stainless steel. Hence to estimate the wear properties and effect of intermetallic and secondary phases in such environment, the wear test was conducted in the atmosphere of artificial ocean water prepared as per the ASTM standard D1141-98. The friction force acting on the pin is directly proportional to the amount of wear it causes. Measurement of friction force and wear in microns during the course of the pin on disc wear test also presents the same effect of precipitation of intermetallic and secondary phases in the specimens. The specimen in as received condition has the maximum friction force acting over it, whereas in case of sigma phase precipitated specimen (875-180) has the least magnitude of friction force. Specimens with the precipitation of chi and α' precipitation lies in the intermediate level. This effect of secondary phases on friction force is depicted in Figure 5.75 where the friction force generated while the specimen was subjected to wear test in the environment of 3.5% NaCl solution is presented.

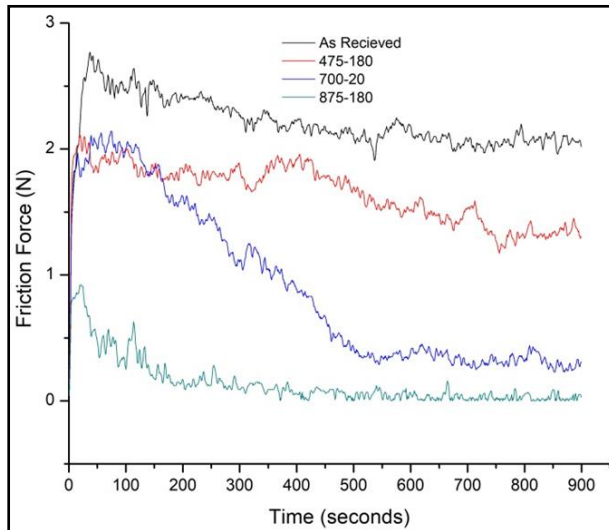


Figure 5.75: Friction force acting on pin specimen in the environment of 3.5% NaCl solution

Similar is the trend of wear measured in microns with respect to time. The maximum wear is observed in the as-received condition of the specimen. Heat treatment improves the wear resistance considerably. The loss of material decreases with the exposure to the heat treatment which leads to precipitation of several secondary phases. Figure 5.76 represents the wear in the specimen as obtained in 3.5% NaCl solution.

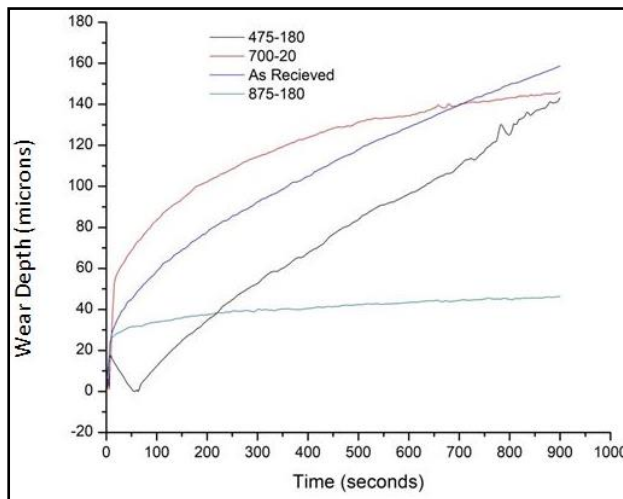


Figure 5.76: Wear in the environment of 3.5% NaCl solution

Wear is basically a progressive loss of material from the contacting surfaces. The wear of material progresses in stages. The initial stage is the change of dimension which further moves onto the change in the geometry. This distortion is a gradual process and finally leads to a considerable loss in weight. The loss of material from the contacting surface changes the dimension of the contacting part. This change in dimension leads to an increased clearance between the two moving parts. Hence the contacting part with changed dimension and geometry contributes significantly to the material loss. In this experiment, the mechanism of progressive wear has been observed and validated using the loss in weight of pin specimen with the increasing sliding distance. Increase in sliding distance increases the metal's weight loss. Initially, at the low sliding distance, the hard metal surface resists the metal removal; hence the loss in weight is quite low. But as the sliding distance increases and the pin is made to slide the distance of 1500m and 2000m, the hard outer layer is removed and there is a rapid increase in the weight loss. Upon reaching the high sliding distance of 3000 m, the pin's wear face has an increased diameter with a new geometry and its contact surface area with the disc increases,

hence the material removal increases which in turn accelerates the weight loss appreciably. Figure 5.77(a-d) represents the obtained weight loss with the changing sliding distance and it follows the above-mentioned pattern.

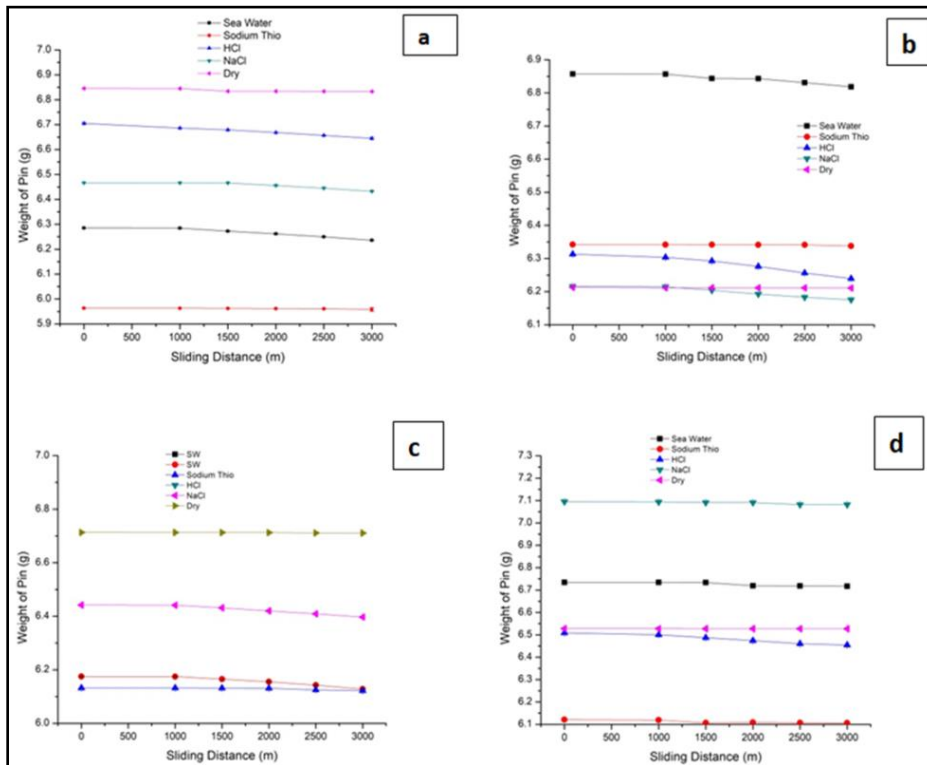


Figure 5.77: Weight Loss with changing sliding distance for specimen: (a) As Recieved (b) 700-20 (c) 475-180 (d) 875-180

The wear data obtained as a loss in the material in microns also reveals the same pattern. The wear for the initial sliding distances is less as compared to the higher sliding distances. As the sliding distance increases, the wear increases multiple folds. Figure 5.78 represents comparative wear of the specimen in the environment of 1M HCl solution.

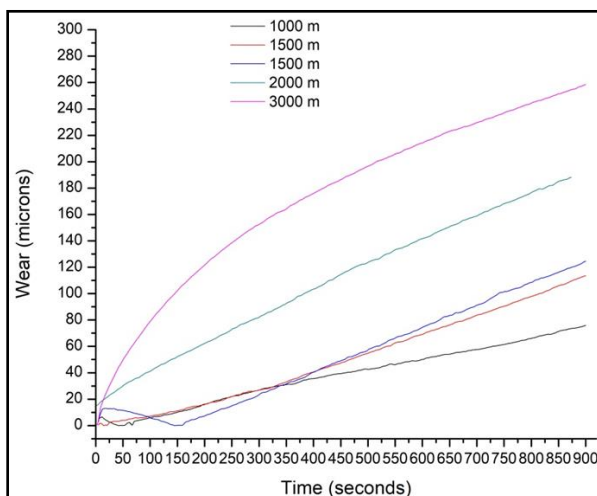


Figure 5.78: Progressive wear with increasing sliding distance in 1M HCl solution

The specimens were investigated for wear mechanism by examining pin's work surface using the scanning electron microscope (SEM). Edge of the cross-section shows that the material has been pushed outwards from the centre and it appears to have formed a bulge on the boundary indicating ploughing mechanism. This pushing out of material from the center along with

cracks developed indicates ductile abrasive wear. As the sliding distance increases to 3000m, the cracks become large enough to grow out. They come out of the surface and appear as spalling and flaking as shown in Figure 5.79.

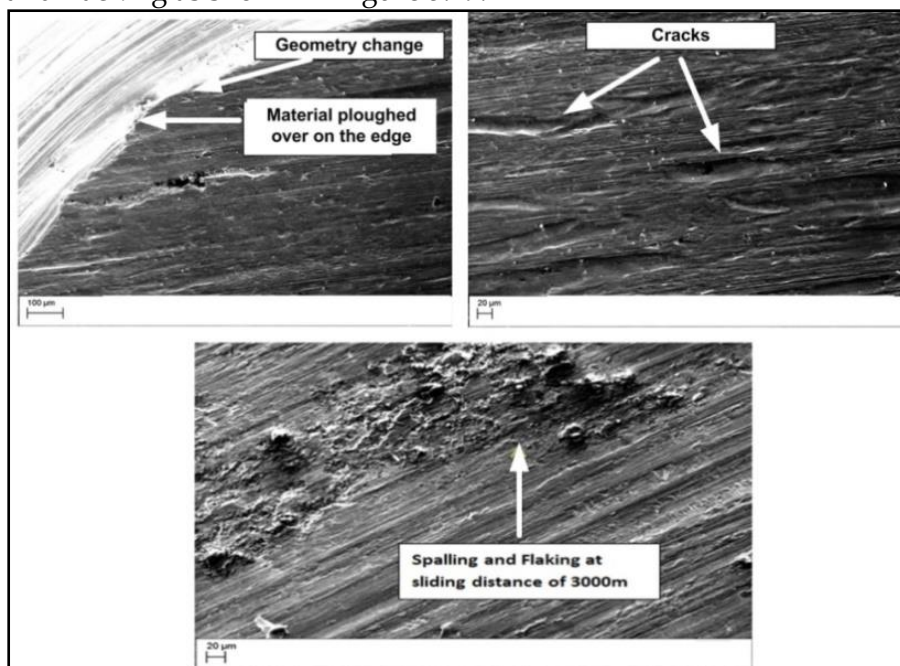


Figure 5.79: Wear mechanism

5.7.2. CORROSION BEHAVIOR INVESTIGATIONS OF SUPER DUPLEX STAINLESS STEEL 2507

The super duplex stainless steel 2507 specimen was heat treated at a temperature of 875°C for 180 minutes followed by air cooling. This was done to precipitate the σ phase in it based on time-temperature-transformation (TTT) diagram. The corrosion resistance of this specimen was compared with super duplex stainless steel 2507 in as received state and pipeline steel API X70. The specimens were subjected to cyclic dry and wet immersion corrosion test in 3.5% NaCl solution and artificial ocean water. Three specimen of each type was taken so as to compare and report the mean value of corrosion property parameters. The specimens were exposed to alternate wet-dry cyclic condition of 24 hour duration each. Relative humidity [RH%] during the experiment was in the range of 70-75. No additional aeration or agitation was employed on the test solutions. The solution was changed before every wet cycle. The test specimens were weight for quantifying the weight loss after 8, 16, 24 and 36 days of observation. Before every weighing, the specimen was cleaned using solutions listed in Table 5.30 as per the ASTM standard [ASTM G1].

Table 5.30: Cleaning solution for cyclic immersion corrosion specimen

Specimen	Solution	Time (min)	Temperature (°C)
API X 70 Steel	500 ml HCL 3.5g Hexamethylene tetramine Reagent Water to make 1000 mL	10	20 to 25
Super duplex 2507 steel	100 ml HNO ₃ 20 mL Hydrofluoric Acid Reagent Water to make 1000 mL	5 - 20	20 - 25

After cleaning the samples were air dried using hot air gun and wiped to remove any unwanted impurity that may have stick to its surface. The specimens were then weighed on an electrochemical balance having a resolution of ± 0.1 mg. Three samples of each specimen was subjected to cyclic immersion test and average value has been reported. Specimens after being

subjected to cyclic immersion test were examined visually to look for surface damage caused due to corrosion. Figure 5.81(a-c) and Figure 5.82(a-c) represents the specimens after they have been subjected to cyclic corrosion dry-wet cycle for 44 days in NaCl solution and artificial ocean water respectively. Visual examination clearly reveals that the extent of corrosion in X70 steel is much more as compared to the super duplex 2507 steel. Super duplex stainless steel with its pitting resistance equivalent number greater than 40 stand out to be an excellent replacement for pipeline steel in the harsh environment locations such as splash zone. Precipitation of σ sigma phase owing to exposure of super duplex steel to high temperature in manufacturing processes for a considerable time period has a negative effect on the corrosion resistance. Corroding environment of NaCl and artificial ocean water cause significant damage to the surface of X70 steel, whereas in the case of super duplex steel, the damage to the steel is mostly in the form of a thin film deposition.



Figure 5.80: Corroded specimens in 3.5% NaCl solution (a) X70 steel (b) As Received SDSS (c) 875-180 SDSS

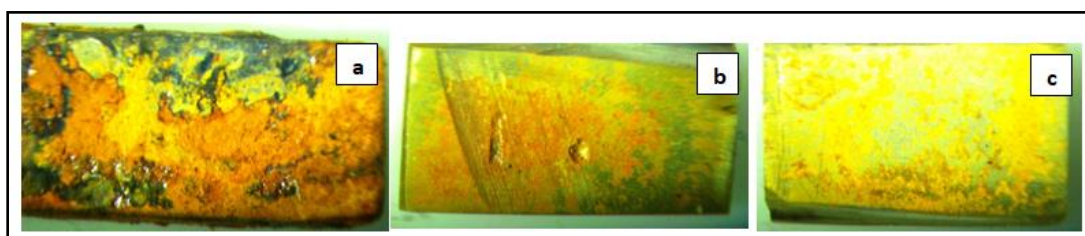


Figure 5.81: Corroded specimens in artificial ocean water: (a) X70 steel (b) As Received SDSS (c) 875-180 SDSS

The specimens subjected to cyclic immersion were weighed in order to find the change in weight that has occurred due to exposure to 3.5% NaCl solution and artificial ocean water. The loss in weight thus obtained was used to calculate the corrosion rate using the equation 5.8:

$$\text{Corrosion Rate} = \frac{K \times W}{A \times T \times D} \quad (5.8)$$

Where, K is a constant whose value is 8.76×10^4 for corrosion rate in units of mm/year, T is time of exposure in hours, A is the exposed area in cm^2 , W is weight loss measured in grams and D represents density of exposed material in g/cm^3 . The results of loss in weight and corresponding corrosion rate indicate that X70 steel is most susceptible to pitting corrosion, whereas super duplex 2507 steel has appreciable corrosion resistance. Precipitation of sigma phase due to the exposure to 875°C for 180 minutes reduces the corrosion resistance. The values of corrosion rate as obtained using weight loss due to cyclic corrosion in represented in Table 5.33.

Table 5.31: Corrosion Rate in cyclic immersion

Specimen/Medium	Corrosion Rate (mm/yr)	
	3.5% NaCl solution	Ocean Water
X 70 Steel	0.60637	0.75561
As Received 2507 Steel	0.02481	0.0324
σ precipitated 2507 Steel	0.0420	0.06034

The results obtained from the cyclic immersion corrosion test of pipeline steel X70 and super duplex stainless steel in as received and heat treated condition clearly indicates the superior corrosion resistance of super duplex steel as compared to pipeline steel. But also, the heat

treatment carried out to precipitate σ phase in super duplex stainless steel, lowers its corrosion resistance. Also, the corrosive action of artificial ocean water was found to be marginally superior as compared to 3.5% NaCl solution.

Summary of Chapter 5:

This chapter presented results of various experimental investigations performed in this study. Sequential methodology of SMAW electrode development and its characterization has been proposed and performed. Performance assessment of laboratory developed electrodes has been done by fabricating and characterizing dissimilar weld between pipelines steel API X70/super duplex stainless steel 2507. A joint between the said base metals has also been fabricated using GTAW process employing two candidate fillers: (i) ASS 309L and (ii) SDSS 2594. Corrosion characterization of GTA welds has been done to correlate it with microstructure and compare the corrosion resistance of different zones in the dissimilar weld. A comparison and suitability assessment has been drawn between the two filler metals used in GTAW process. An attempt has also been made to characterize the properties of mining waste red ochre and its direct utilization in welding consumable development in the as-is state. Experimental results quantify the effect of heat treatment on wear and corrosion behavior of super duplex stainless steel in actual service environment simulated at laboratory level.