

This chapter describes the regression analysis, model comparison, and effect of flux constituents for various flux and BOP characterization. Characteristics of the selected fluxes was then given. Mechanical, metallurgical test and hydrogen charging results of the welds were discussed. Finally, ductile fracture experiments were analyzed. GTN model parameters were identified and its validation was performed on different geometries.

5.1 CHARACTERIZATION OF FLUX COATINGS AND BOP

5.1.1 High temperature wettability

(a) Regression analysis of the wettability properties

The regression analysis was performed on the wetting behavior attributes such as contact angle (θ), spreading area (A_s), work of adhesion (W_a), and floatation coefficient (Δ). The values of γ_s are the surface tension of the complete electrode coating having oxides, fluorides, deoxidizer, and iron powder at 1573 K. The surface tension was calculated using the equations given in experimentation section. The calculations of W_a and Δ was done by employing γ_s only, however, $(\gamma_s)_{\text{flux}}$ is calculated only for the sake of completeness. The values of $(\gamma_s)_{\text{flux}}$ are the surface tension of the oxide and fluoride melts at 1573 K. The mole fractions were adjusted accordingly. The wetting properties, Λ^{corr} and BI of both the flux systems are given in Table 5.1 and 5.2.

The regression models were developed for the θ , A_s , W_a , and Δ . The regression models are fitted with quadratic and special cubic since the higher order interaction was expected due to the complex nature of the multi-component systems. Regression model and ANOVA table is given in the appendix Table A1-A4. In ANOVA analysis, the F-value of the models shows that the signal is stronger than the noise. The P-values of the models are less than 0.05, which indicates that the models are significant.

Table 5.1: Wetting properties and corrected optical basicity of different flux compositions (AF flux)

Flux no.	θ	A_s	W_a	Δ	γ_s	$(\gamma_s)_{\text{flux}}$	Λ^{corr}	BI
AF1	70.12	141.39	1.281	0.631	956.26	455.68	0.805	3.00
AF2	86.40	186.32	1.003	0.885	943.73	433.31	0.808	3.00
AF3	72.95	189.63	1.253	0.685	969.29	470.34	0.737	2.17
AF4	62.83	199.38	1.415	0.528	971.62	463.03	0.797	3.00
AF5	62.75	199.25	1.415	0.526	970.73	465.65	0.766	2.55
AF6	63.58	242.26	1.396	0.537	966.49	463.78	0.736	2.17
AF7	78.88	207.67	1.144	0.774	959.38	453.93	0.776	2.62
AF8	85.09	196.22	1.034	0.871	952.68	448.98	0.765	2.44
AF9	65.29	208.67	1.337	0.549	943.05	437.92	0.809	3.00
AF10	64.26	212.78	1.391	0.549	969.82	468.31	0.735	2.17
AF11	72.72	207.78	1.261	0.683	972.36	459.32	0.763	2.55
AF12	84.79	188.66	1.029	0.858	943.19	436.03	0.803	2.92
AF13	66.32	245.09	1.349	0.576	962.65	461.33	0.738	2.17
AF14	67.16	236.72	1.329	0.586	957.43	455.93	0.775	2.59
AF15	67.29	242.25	1.327	0.588	957.55	449.31	0.803	3.00

AF16	81.71	200.48	1.079	0.807	943.39	435.64	0.808	3.00
AF17	75.35	238.93	1.181	0.704	942.92	437.38	0.801	2.88
AF18	70.27	205.60	1.294	0.641	967.43	465.98	0.736	2.17
AF19	73.02	161.56	1.239	0.679	958.68	449.87	0.772	2.59
AF20	76.52	154.76	1.195	0.743	969.16	471.64	0.769	2.55
AF21	70.95	198.74	1.272	0.646	958.90	442.56	0.800	3.00
AF22	66.15	214.52	1.363	0.578	970.35	466.25	0.734	2.17
AF23	75.82	224.24	1.203	0.729	965.98	465.85	0.737	2.17
AF24	78.32	231.10	1.134	0.752	943.26	435.07	0.800	2.88
AF25	73.27	258.47	1.248	0.690	969.03	472.87	0.801	3.00
AF26	78.47	186.34	1.131	0.754	942.80	436.83	0.792	2.76
AF27	69.99	235.07	1.308	0.641	974.39	452.23	0.793	3.00

Table 5.2: Wetting properties of different flux compositions and corrected optical basicity (SF flux)

Flux no.	θ	A_s	W_a	Δ	γ_s	$(\gamma_s)_{\text{flux}}$	Λ^{corr}	BI
SF1	57.23	260.1	1.502	0.447	974.40	452.23	0.793	3.00
SF2	84.27	175.0	1.064	0.871	967.64	460.05	0.817	3.36
SF3	82.78	175.2	1.048	0.814	931.04	414.03	0.759	2.20
SF4	79.02	208.9	1.121	0.763	941.95	419.37	0.787	2.69
SF5	71.74	174.1	1.263	0.661	962.01	443.00	0.856	4.33
SF6	75.67	200.6	1.185	0.715	950.28	425.38	0.749	2.20
SF7	74.76	226.4	1.227	0.716	971.63	463.04	0.797	3.00
SF8	68.24	210.1	1.346	0.618	981.61	455.30	0.848	4.33
SF9	80.02	170.3	1.123	0.791	957.32	428.01	0.798	3.00
SF10	103.80	129.1	0.708	1.152	929.77	426.38	0.764	2.20
SF11	81.55	222.6	1.074	0.799	936.28	428.83	0.811	3.00
SF12	83.32	180.7	1.114	0.882	997.94	478.80	0.842	4.33
SF13	75.25	190.9	1.196	0.710	953.01	451.30	0.806	3.00
SF14	96.84	141.0	0.804	1.021	912.31	403.27	0.768	2.20
SF15	68.84	199.3	1.276	0.599	937.80	416.39	0.807	3.00
SF16	76.01	222.8	1.186	0.724	955.09	440.22	0.802	3.00
SF17	71.15	199.3	1.295	0.662	978.56	466.14	0.850	4.33
SF18	109.90	108.9	0.618	1.255	936.39	426.06	0.759	2.20
SF19	70.01	213.1	1.295	0.635	964.74	450.93	0.781	2.69
SF20	68.91	220.6	1.321	0.622	971.18	445.25	0.812	3.36
SF21	72.32	188.4	1.225	0.654	939.75	435.56	0.793	2.69
SF22	74.73	232.6	1.194	0.696	945.32	429.42	0.824	3.36
SF23	75.61	178.3	1.198	0.721	959.67	454.13	0.859	4.33
SF24	81.06	189.5	1.096	0.801	948.32	437.52	0.755	2.20
SF25	45.40	206.9	1.658	0.290	974.06	454.89	0.852	4.33
SF26	82.43	181.1	1.071	0.822	946.49	448.56	0.760	2.20
SF27	70.32	221.7	1.289	0.640	964.52	430.72	0.854	4.33

(b) Statistical comparison of regression and ANN models of wettability properties

In the sections (b) statistical comparison of regression and ANN model and (c) effect of flux compositions, have been discussed only for the AF flux system to avoid repetitiveness.

The Levenberg-Marquardt backpropagation algorithm was used to train the model. In the learning process of backpropagation, errors are propagated backward through the network to

tune the weights and thresholds between layers, minimizing the mean squared error of the output. The training of the model for contact angle data required 6 hidden neurons. The overall $MSE_{ANN} = 6.2$ is obtained for the contact angle. The spread area model required 10 hidden neuron layer size to result in an overall $MSE_{ANN} = 126.23$. The model for work of adhesion is found to perform well with 5 hidden neurons, which resulted in $MSE_{ANN} = 0.0027$. The floatation coefficient model needed 8 hidden neurons, which resulted in $MSE_{ANN} = 0.0018$. Table 5.3 shows the ANN model details. The goal was to achieve $MSE_{ANN} < MSE_{RA}$ for the trained dataset and $MAPE_{ANN} < MAPE_{RA}$ for the test dataset. Figure 5.1 shows the comparison of regression analysis (RA) predictions and ANN predictions with actual results. The results show that the fitting capability of ANN model is better than the regression analysis.

Table 5.3: ANN training details for wettability models

Model	N_H	MSE Training	MSE Validation	MSE_{ANN}	R-value Training	R-value Validation	R-value All
θ	6	4.61	13.23	6.206	0.946	0.908	0.933
A_s	10	130.18	108.85	126.23	0.929	0.590	0.916
W_a	5	0.0023	0.0045	0.0027	0.921	0.833	0.903
Δ	8	0.0004	0.0081	0.0018	0.983	0.757	0.922

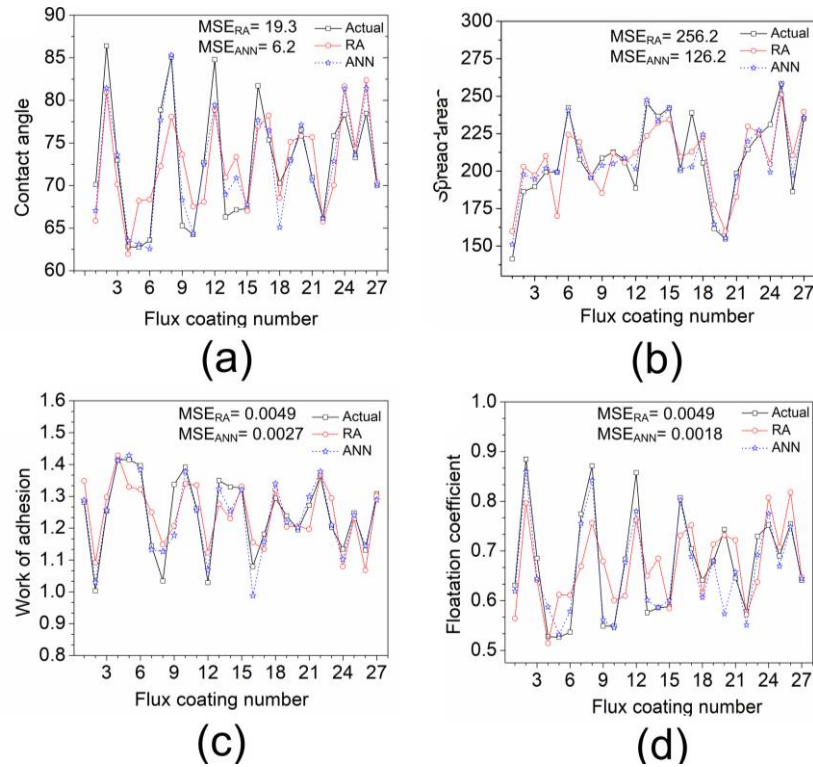


Figure 5.1: Comparison of regression analysis (RA) prediction and ANN prediction with actual results (a) contact angle (b) spread area (c) work of adhesion (d) floatation coefficient

An overfitted model only has very good prediction accuracy for trained data, whereas this accuracy lacks for unseen data sets. The unseen test data is used to confirm that the model is not overfitted. The composition used as the test data set is given in Table 5.4. Table 5.5 shows the mean absolute percentage error of the regression analysis (RA) and ANN prediction. The results suggest that the ANN models are appropriate and capable of predicting unseen data better than the regression analysis prediction. The use of both methods has its pros and cons. The joint applicability of both methods can complement each other (Freiesleben et al., 2020). It can be concluded that the use of the regression analysis approach is easier and provides more insight into the experiments, whereas the ANN model lacks due to its complex nature. The

ANN model has better modeling and prediction capability than the regression analysis due to its robust structure.

Table 5.4: Test dataset for AF flux system

#	Flux	CaF ₂	CaO	Al ₂ O ₃	BaO
1	VAF1	31.63	18.88	13.63	5.88
2	VAF2	33.43	17.28	13.43	5.88
3	VAF3	35.63	15.88	12.13	6.38

Table 5.5: Mean absolute percentage error (MAPE) of RA and ANN prediction on the test data set

#	Actual value	RA prediction	ANN prediction	MAPE _{RA}	MAPE _{ANN}
θ	75.7	71.58	81.45	7.20	4.39
	67.5	72.78	68.29		
	70.5	76.38	73.60		
A_s	187.7	212.48	197.74	10.92	10.24
	194.5	227.51	203.89		
	213.9	208.33	257.88		
W_a	1.212	1.270	1.054	6.80	5.93
	1.344	1.243	1.322		
	1.280	1.176	1.238		
Δ	0.732	0.659	0.859	10.78	9.03
	0.589	0.674	0.561		
	0.638	0.727	0.670		

(c) Effect of flux compositions on wettability properties

The effect of flux compositions on the contact angle (θ)

The contact angle measures the wetting of a liquid such as molten slag on the metal surface. The low contact angle indicates higher surface energy, i.e., high interfacial tension. The contact angle depends on the molecular activity at the interface of slag and metal. The wetting properties such as surface tension and contact angle are highly dependent on the surface monolayer activity rather than the bulk activity. The contact angle is dependent on the constituents, temperature, and interfacial contact. The trace plot is shown in Figure 5.2 (a). The trace plot suggests the individual effect of the constituents on the contact angle. The contact angle is found to decrease with the increase of CaO and BaO. These constituents are known as network breakers because they reduce the number of bridging oxygen O^0 and increasing the non-bridging oxygen O^- (Kim et al., 2016). The contact angle is found to increase and decrease with the increase of Al_2O_3 . The Al_2O_3 is involved in the network formation with the fluorides $[AlO_nF_{4-n}]$ ($n = 0 - 4$) (Park et al., 2002). The contact angle increases with the increase of the CaF_2 . The general network modification theory suggests that the acidic oxides (Al_2O_3 , SiO_2) act as network formers, and basic oxide (CaO, BaO) act as network breaker. The role of CaF_2 is generally agreed as a network breaker for lower concentrations. According to the current results CaF_2 should be present in the melt as Ca^{2+} , F^- due to higher CaF_2 concentration (~35%). The activity of F^- near the interface of Fe^{2+} cation has Van der Waals forces which may have a substantial influence on the contact angle. The role of CaO and BaO can be explained as network breakers hence reducing the contact angle. The contact angle decreases as the increase of binary interaction of CaO.BaO, and CaF_2 .CaO whereas, CaF_2 . Al_2O_3 and CaO. Al_2O_3 has a moderate increasing effect on the contact angle.

The effect of flux compositions on the spread area (A_s)

The regression model of the spread area suggests that the interaction of higher order is more prominent. The spread area is inversely related to the contact angle. The binary interaction

of the CaF_2 .CaO, CaF_2 . Al_2O_3 , CaF_2 .BaO, and CaO. Al_2O_3 has a decreasing effect on the spread area. The ternary interaction of CaF_2 .CaO. Al_2O_3 , and CaF_2 .CaO.BaO has an increasing effect on the spread area. The spread area depends on the ability of the molten pellet to withstand the force of gravity. The spread area increases as the contact angle decreases.

The effect of flux compositions on the work of adhesion (W_a)

Figure 5.2 (b) shows the trace plot of the work of adhesion. The work of adhesion is the energy required to separate two phases, viz., slag and metal. The lower contact angle leads to higher work of adhesion due to improved wetting; this can also be confirmed by comparing the trace plot of contact angle and work adhesion in Figure 5.5 (a) and (b). The increase of CaO and BaO is found to have an increasing effect on the work adhesion, whereas, an increase of the CaF_2 decreases the work of adhesion. The work of adhesion decreases and then increases with Al_2O_3 . The work of adhesion is found to increase with the increase of the binary mixture CaO.BaO, and CaF_2 .CaO.

The increase and decrease in the physical properties of molten slag can be understood by the network modification theory. The network formed by Al_2O_3 and SiO_2 in which the oxygen is predominantly bridging oxygens (O^0) are tend to break when network breakers such as CaO and BaO which are rich in free oxygen (O^{2-}) and forms non bridging (2O^-) (Seetharaman, 2005). The Al_2O_3 is involved in the network formation with the fluorides $[\text{AlO}_n\text{F}_{4-n}]$ ($n = 0 - 4$) (Park et al., 2002). The addition of fluorides initially act as network breaker till the exhaustion of $[\text{SiO}_4]$ – tetrahedral units and $[\text{AlO}_4]$ – tetrahedral units. Once the silicate and aluminates exhausted the activity of F^- near the interface of Fe^{2+} cation has Van der Waals forces which may have a substantial influence on the contact angle. The contact angle and work of adhesion are inversely correlated. The characterization of slag are given in more details in the section 5.1.4 (b) structural properties.

The effect of flux compositions on the floatation coefficient (Δ)

The floatation coefficient is the difference between the work of cohesion and the work of adhesion. The trace plot in Figure 5.2 (c) indicates that the Δ increases with increase of CaF_2 , and Al_2O_3 . The increase of individual constituents CaO and BaO has a decreasing effect on the Δ . The Δ is found to decrease with the increase of binary interaction of CaO.BaO, and CaF_2 .CaO. The increase of CaO.BaO, and CaF_2 .CaO increases the work of adhesion. The work of cohesion is twice the surface tension which is dependent on the mole fraction and the surface tension of the individual constituents. Overall, the difference between the work of cohesion and the work adhesion reduces with the increase of CaO.BaO, and CaF_2 .CaO.

The cleanliness of a weld significantly depends on the removal of inclusions from the molten weld pool, primarily through buoyancy and flotation mechanisms. Gases generated during welding and low-density inclusions tend to float to the surface of the molten metal. This separation is governed by interfacial phenomena between the molten metal and slag inclusions, which are quantified by the flotation coefficient. A positive flotation coefficient indicates the potential for inclusions to attach to rising gas bubbles and separate from the weld pool. However, while necessary, a positive flotation coefficient alone does not guarantee complete inclusion removal, making interfacial behavior critical (Seetharaman, 2005).

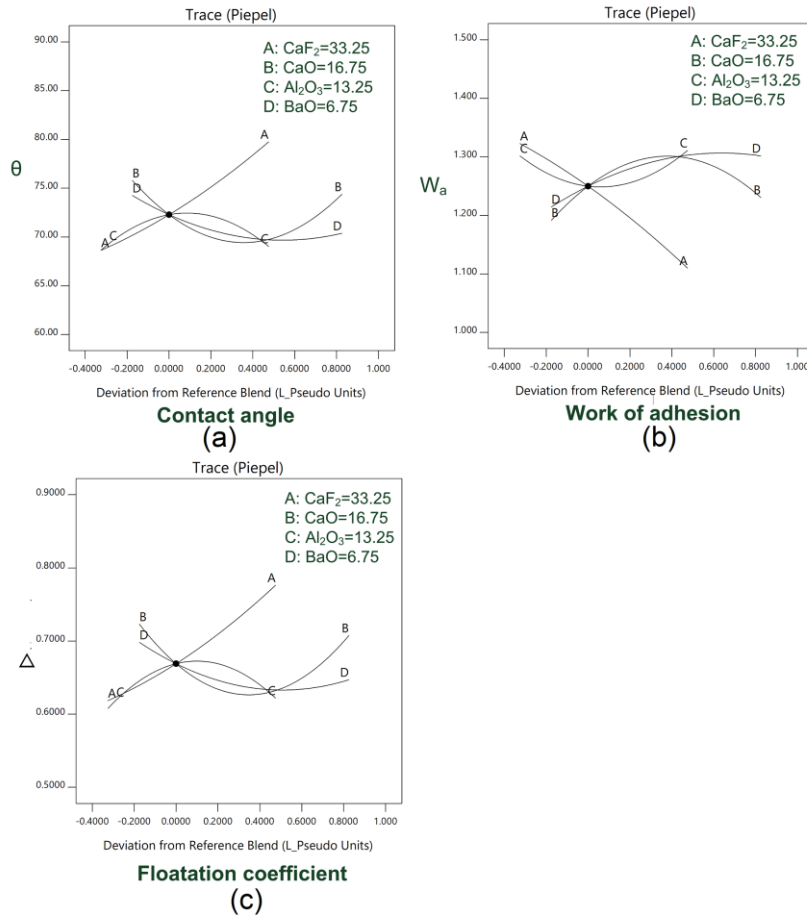


Figure 5.2: Trace plot of the regression model of (a) contact angle (b) work of adhesion (c) floatation coefficient

The contour plots of the wetting properties θ , A_s , W_a , and Δ are shown in Figure 5.3. The contour plots show the continuous variation of the properties which occurs due to the variation of the input parameter. Each color scheme represents a distinct set of values.

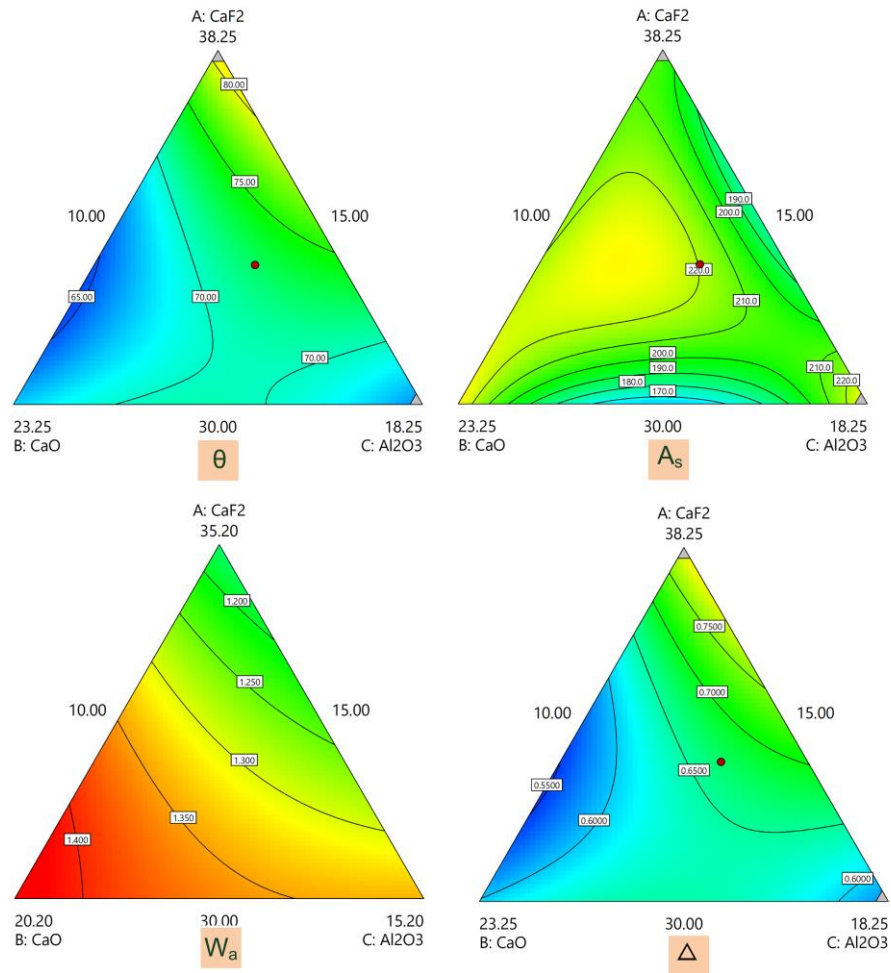


Figure 5.3: The contour plots of the wetting properties θ , A_s , W_a and Δ

5.1.2 Thermophysical and physicochemical properties

(a) Regression analysis of the thermophysical and physicochemical properties

The thermal stability of the fluxes during heating is revealed by the TGA analysis. The weight change is recorded while the fluxes are heated; depending on the nature of the compounds, the weight change could be a gain or loss. Weight loss is typically caused by evaporation, reduction, and decomposition, whereas weight gain is caused by oxidation and adsorption. Figure 5.4 (a), (b). shows the TGA curves of the fluxes. The thermogravimetry (TG) curve shows weight loss while heating at a constant rate, and a derivative of thermogravimetry (DTG) curve marks the presence of significant thermodynamic event. Initially, a gradual weight loss is recorded up to $\sim 500^\circ\text{C}$, this weight loss has occurred due to the loss of moisture, water of crystallization and other volatile compounds present in the mineral. The second major thermal response recorded by the DTG curve can be seen from 600°C - 750°C , this event is the calcination of calcite present in the flux (El-Sadek et al., 2019). Weight gain has been caused by the high-temperature oxidation of iron powder in the flux after 750°C . The thermal stability of the flux is determined by the weight loss caused by the loss of moisture content, volatile compounds, water of crystallization, and mineral calcination. Except for calcination, the remainder of the weight loss results in gaseous infiltration in the weld and no shielding.

Figure 5.4 (c), (d) shows DSC curve of the coating fluxes AF13 and AF17. The initial downward trend of the heat flow curve suggests flux is endothermic in nature. As the temperature rises, the final stage shows a slightly upward trend due to exothermic reactions at high temperatures. The DSC curve records the heat flow in the flux as compared with reference material. DSC results suggest flux heating involves three distinct thermal events. The first event

is the loss of moisture at around $\sim 100^{\circ}\text{C}$, second event show the loss of crystallization water and volatile compounds of minerals ($200^{\circ}\text{C} - 500^{\circ}\text{C}$) and the third event is the calcination of the calcite ($600^{\circ}\text{C} - 750^{\circ}\text{C}$), in the third step, carbonates decompose to CaO . The area under the curve represents the amount of change in the system's enthalpy while heating. The enthalpy change is determined by the constituents. The TGA-DSC analysis shows the relationship between "weight loss" and "enthalpy." The loss of moisture, crystallization water, and calcination are associated with weight loss as well as the change in enthalpy.

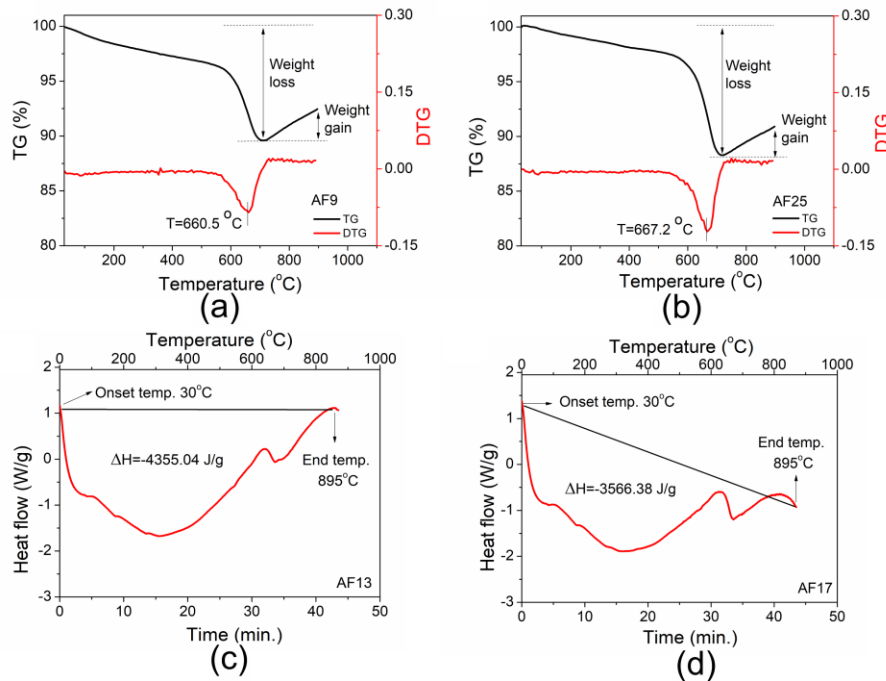


Figure 5.4: (a) (b) TGA curve of the coating fluxes AF9 and AF25, (c) (d) DSC curves of the coating fluxes AF13 and AF17

The regression analysis was performed to model the thermal properties of flux, such as weight loss (WL), enthalpy (ΔH), conductivity (λ), diffusivity (α), and specific heat (C_p). Table 5.6 and Table 5.7 summarizes the response data from the TGA-DSC and hot disk analysis for both the flux systems. The regression models and ANOVA analysis is given in appendix Table A5-A8. In the ANOVA analysis, the P-values of the models are less than 0.05, indicating statistical significance. Furthermore, the F-values demonstrated that the signal is stronger than the noise.

Table 5.6: TGA-DSC and hot disk analysis results (AF flux)

Flux	WL (%)	ΔH (J/g)	λ (W/mK)	α (mm^2/s)	C_p (J/gK)
AF1	10.04	-5033.3	1.3820	1.0020	0.7385
AF2	8.49	-2792.5	1.2001	0.8499	0.7715
AF3	10.41	-7257.8	1.3130	0.8707	0.7520
AF4	8.53	-1744.6	1.0600	1.1310	0.4575
AF5	12.25	-7786.0	0.9184	1.1060	0.4209
AF6	11.01	-5711.0	1.3250	0.8822	0.8458
AF7	9.54	-2815.8	1.1190	0.7192	0.7718
AF8	9.15	-5489.2	1.2090	1.3850	0.4495
AF9	10.35	-4341.0	0.9451	1.2030	0.4023
AF10	10.24	-7388.1	1.4270	1.1950	0.5902
AF11	11.37	-5496.2	1.1170	1.4010	0.4130

AF12	10.29	-5304.6	1.1720	1.4110	0.4315
AF13	9.12	-4355.0	1.5580	1.2630	0.6649
AF14	10.44	-4530.3	1.2928	1.4000	0.4363
AF15	10.09	-4702.7	1.3630	0.7870	0.8096
AF16	9.98	-5001.8	1.1830	0.9908	0.5970
AF17	9.79	-3566.4	1.1460	1.0860	0.5555
AF18	9.44	-4026.6	0.9613	1.2040	0.4081
AF19	10.97	-1076.7	1.2090	1.1510	0.4968
AF20	10.90	-5350.1	1.2040	0.7310	0.7858
AF21	9.98	-3307.7	1.4470	0.9095	0.8593
AF22	11.48	-7575.7	1.2570	1.0630	0.6229
AF23	8.79	-3351.4	1.6020	0.8220	0.9340
AF24	10.39	-3159.3	0.7915	1.1100	0.3981
AF25	11.69	-4771.5	1.2660	0.7585	0.8271
AF26	9.38	-3093.0	1.4470	1.0540	0.6350
AF27	11.05	-6946.4	2.1546	1.4007	0.7555

Table 5.7: TGA-DSC and hot disk analysis results (SF flux)

Flux	WL (%)	ΔH (J/g)	α (mm ² /s)	λ (W/mK)	C_p (J/gK)
SF1	10.28	-3456.5	0.938	1.449	0.7421
SF2	9.58	-2955.6	1.016	1.371	0.6970
SF3	8.32	-3248.8	1.158	1.000	0.4448
SF4	8.00	-3503.1	1.272	1.401	0.5254
SF5	9.51	-2671.3	1.488	1.227	0.4318
SF6	7.73	-5145.1	1.293	0.951	0.3818
SF7	12.32	-3499.3	1.405	1.272	0.4685
SF8	9.83	-3956.1	0.867	1.295	0.7132
SF9	9.08	-6004.5	0.812	1.128	0.7173
SF10	7.81	-3602.0	1.297	1.120	0.3648
SF11	9.48	-4161.3	2.050	1.480	0.3738
SF12	11.30	-4117.7	2.556	1.208	0.2384
SF13	11.02	-3444.6	1.096	1.393	0.6346
SF14	7.40	-5756.3	1.329	1.242	0.4852
SF15	7.25	-6995.7	1.626	1.420	0.4041
SF16	9.46	-3502.4	1.391	1.334	0.4699
SF17	12.35	-5303.3	1.204	1.310	0.5454
SF18	8.19	-3025.8	1.562	1.041	0.2359
SF19	9.88	-3682.8	1.321	1.271	0.4861
SF20	10.79	-2989.8	1.075	1.247	0.5592
SF21	10.05	-5040.3	1.386	1.615	0.6239
SF22	8.95	-6028.9	1.168	1.288	0.5229
SF23	11.15	-4793.9	1.554	1.424	0.4408
SF24	9.11	-3436.6	1.037	1.415	0.4531
SF25	10.34	-3540.4	1.526	1.092	0.5640
SF26	11.02	-4607.2	1.789	1.374	0.3664
SF27	10.18	-7387.0	1.676	1.074	0.3090

(b) Statistical comparison of regression and ANN models of thermophysical and physicochemical properties

Table 5.8 shows the ANN model details, Figure 5.5 shows ANN models fitting capability as compared with regression analysis. The R-values of the training data and validation data are between 0.77 and .95 which shows a strong correlation. For all the models, the average improvement in MSE for a trained model is nearly 37%. It is evident that the ANN model outperforms the regression model in terms of fitting.

Table 5.8: ANN training details for thermophysical and physicochemical models

Model	N_H	MSE Training	MSE Validation	MSE_{ANN}	R-value Training	R-value Validation	R-value All
WL	8	0.1454	0.3994	0.1924	0.9266	0.9251	0.8979
ΔH	9	6.504E4	1.344E6	3.019E5	0.9888	0.8317	0.9493
λ	7	0.0199	0.0025	0.0166	0.8664	0.8501	0.8650
α	5	0.0124	0.0146	0.0128	0.8576	0.8463	0.8562
C_p	5	0.0091	0.0243	0.0119	0.8175	0.8112	0.7709

The prediction accuracy of an overfitted model is excellent only for predictors used for training data, not for unseen data. The trained model is subject to unseen or test data to confirm its efficacy. The test dataset is shown in Table 5.4. The MAPE of regression analysis (RA) and artificial neural network (ANN) predictions is shown in Table 5.9. The MAPE value of weight loss prediction with RA is 7.06 %, which is reduced to 4.69 % with ANN. The MAPE value of enthalpy prediction with RA is 27.44 % and with ANN is 11.84 %. The MAPE value of prediction of thermal conductivity, thermal diffusivity is also improved from 12.82 to 11.11% and 17.14 to 13.75 % respectively. Prediction accuracy of specific heat with RA and ANN is 21.72 and 17.03 % respectively.

Table 5.9: Mean absolute percentage error (MAPE) of RA and ANN prediction on the test data set

#	Actual value	RA prediction	ANN prediction	$MAPE_{RA}$	$MAPE_{ANN}$
WL	11.260	10.813	11.298	7.061	4.692
	9.630	10.365	10.209		
	11.110	10.043	10.248		
ΔH	-4841.82	-5068.31	-4463.20	27.440	11.844
	-3012.13	-3805.41	-3651.75		
	-5210.62	-2537.31	-4873.03		
λ	1.287	1.152	1.223	12.820	11.111
	1.366	1.205	1.211		
	1.006	1.169	1.177		
α	0.8018	0.9682	0.7267	17.145	13.752
	0.8767	1.0287	1.0543		
	1.1953	1.0358	1.3343		
C_p	0.7602	0.6582	0.6929	21.725	17.039
	0.8438	0.6212	0.6182		
	0.8092	0.6039	0.6836		

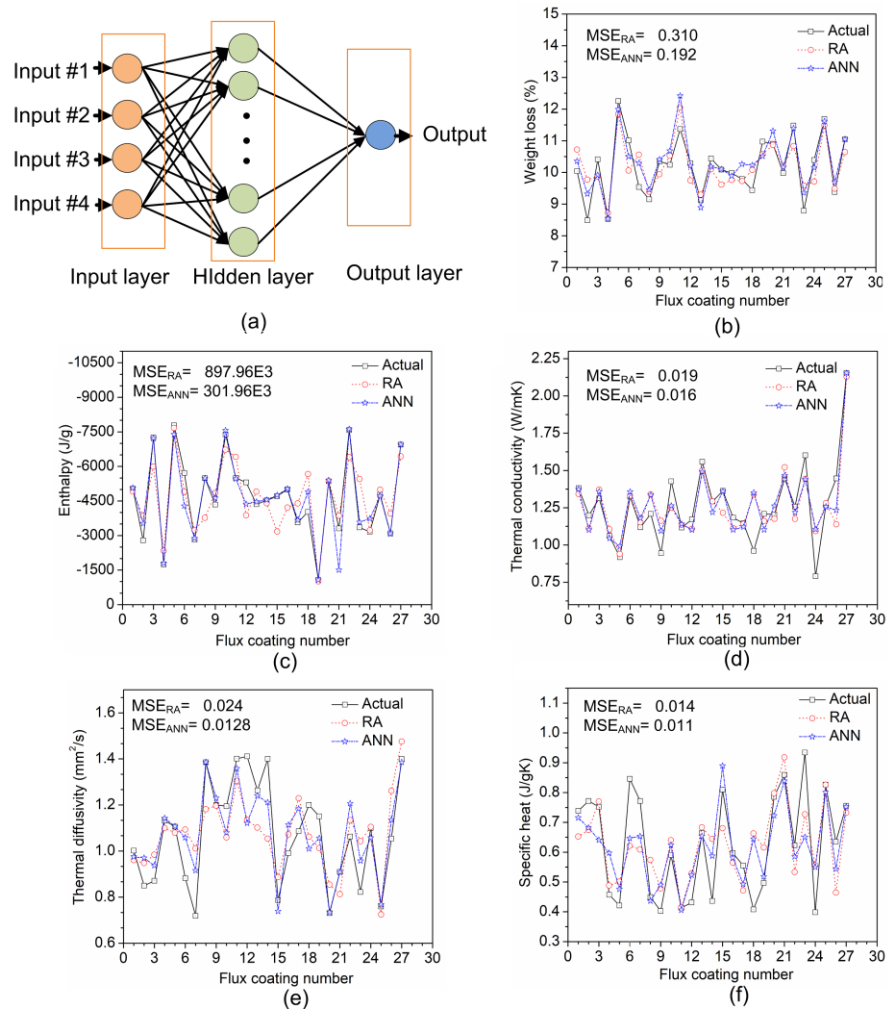


Figure 5.5: (a) Structure of ANN model; comparison of ANN and RA prediction from actual values (b) weight loss, (c) enthalpy, (d) thermal conductivity, (e) thermal diffusivity, (f) specific heat

(c) Effect of flux compositions on thermophysical and physicochemical properties

Effect of Flux Compositions on Weight Loss (WL)

With changes in flux composition, weight loss percentages ranged from 8.49% to 12.25%. Figure 5.6 (a) depicts the regression model's trace plot. The developed regression model shows that CaF_2 has reducing effect on weight loss. Fluorspar is the source of CaF_2 in the fluxes. The results suggest that fluorspar is more thermally stable than other minerals used, which leads to reduced gaseous infiltration. The CaO and BaO has positive effect on the weight loss, these minerals have higher crystallization water and good affinity for moisture. The role of Al_2O_3 is increasing and then decreasing the weight loss. The binary interaction between $\text{CaO}.\text{Al}_2\text{O}_3$, $\text{CaO}.\text{BaO}$, and $\text{Al}_2\text{O}_3.\text{BaO}$ have reducing effect on the weight loss, ternary interaction between $\text{CaO}.\text{Al}_2\text{O}_3.\text{BaO}$ has shown positively affecting the weight loss. Experiments with mixtures often involve synergistic and anti-synergistic interactions, $\text{CaO}.\text{BaO}$ show anti-synergistic effect on the weight loss whereas their individual effects are opposite. Calcite mineral (CaCO_3) is the primary source of CaO in the flux and has a significant impact on weight loss due to calcination and the presence of crystalline water in the mineral. CaO and BaO are basic oxides that refine molten weld pool, their binary interaction produces more thermally stable flux. Previous research also indicates that the addition of BaO improves the acicular ferrite in the weld, which is responsible for improving the mechanical properties (El-Sadek et al., 2019; Wang et al., 2018).

Effect of Flux Composition on Enthalpy (ΔH)

The change in flux composition has resulted in a variation in enthalpy from -1076.7 to 7786 J/g. Figure 5.6 (b) shows trace plot for ΔH . The trace plot shows all individual components have a significant influence on enthalpy change while heating. An increase in CaF_2 reduces variation in enthalpy change, which shows fluor spar is comparatively stable and requires the least amount of heating enthalpy. An increase in CaO and BaO that calcite and witherite have a positive effect on the enthalpy change; the weight loss of these minerals happens at the expense of heating enthalpy. The binary interaction between CaF_2 . Al_2O_3 , CaF_2 . BaO , and Al_2O_3 . BaO has shown negative influence and interaction between CaO . Al_2O_3 , and CaO . BaO has a positive effect on changes in enthalpy. The ternary interaction of CaF_2 . Al_2O_3 . BaO has positive effect, whereas CaO . Al_2O_3 . BaO has negative effect on the enthalpy change. As the temperature rises, the change in enthalpy corresponds to an increase in internal energy. Lower enthalpy change indicates thermal stability of constituents while heating.

The enthalpy of heating in flux coatings is strongly influenced by their mineral composition and the minerals' affinity for moisture and crystallization water. TGA-DSC analysis reveals that weight loss during heating—caused by moisture evaporation, loss of crystallization water, and calcination—correlates directly with enthalpy changes. Minerals with higher moisture content or volatile compounds exhibit greater enthalpy variation due to increased thermal events. The initial endothermic reactions, followed by exothermic behavior at high temperatures, reflect the nature and transformation of mineral phases. Thus, the thermal response and energy required for heating are largely dictated by the flux's mineral constituents and their thermal stability (El-Sadek et al., 2019).

Effect of Flux Composition on Thermal Conductivity (λ)

Thermal conductivity varies from 0.791 to 2.154 W/mK when the flux composition changes. Figure 5.6 (c) shows a positive effect on the thermal conductivity, while calcite has a reducing effect. An increase in witherite content in the flux has shown decreasing and then increasing effect. The alumina has a moderate effect on the thermal conductivity. The binary interaction between CaF_2 . CaO and CaF_2 . Al_2O_3 has an increasing effect on thermal conductivity and CaF_2 . BaO , CaO . Al_2O_3 , CaO . BaO , and Al_2O_3 . BaO have a decreasing effect on thermal conductivity. Thermal conductivity is affected by several factors, including composition, porosity, and moisture content. All of the specimens are prepared in the same manner and then baked for 90 minutes at 623 K which limits the variations in porosity and moisture content. The changes in flux composition cause variations in phonon mean free path and molar heat capacity, resulting in varying thermal conductivity of the coated flux. The phonon mean free path is also affected by temperature, which is held constant in this work (Kang et al., 2014). Higher thermal diffusivity and conductivity carry heat more quickly, which is appropriate for electrode coating.

The thermal properties of flux, which is a baked mixture of various minerals, are significantly influenced by pore structure and moisture content. In SMAW electrodes, coatings with a high number of pores and minerals that readily absorb moisture tend to exhibit higher thermal conductivity, as water conducts heat more effectively than air. Therefore, coatings with smaller pore sizes and lower moisture affinity are more desirable during welding. However, relying solely on the thermal properties of flux coatings can be misleading. It is preferable to select minerals with low moisture affinity, and pore size can be controlled by using finely ground mineral powders in the coating.

Effect of Flux Composition on Thermal Diffusivity (α)

Thermal diffusivity is a measure of how quickly heat waves travel through conduction. Thermal diffusivity values range from 0.719 to 1.411 mm^2/s as a result of flux composition. Figure 5.6 (d). shows the trace plot of thermal diffusivity. An increase in CaF_2 has shown a very mild influence on thermal diffusivity, whereas calcite has shown a decreasing effect on thermal diffusivity. Alumina has shown increasing effect on the diffusivity. An increase in witherite has shown mainly increasing effect on diffusivity after the reference point. The binary interaction of

CaF_2 . BaO has negative effect on diffusivity. It can be observed that calcite, witherite has shown a mainly increasing effect on diffusivity after the reference point. The binary interaction has a negative effect on diffusivity. It can be observed that calcite, witherite, and alumina have major influences on diffusivity. The thermal diffusivity of the coating flow is given by the ratio of heat transferred to heat stored.

Thermal diffusivity increases with higher thermal conductivity and decreases with greater heat capacity. A high diffusivity means the material can rapidly transmit heat away from the source, reflecting efficient heat transfer. Conversely, low diffusivity indicates that heat moves more slowly through the material, as it either has low conductivity or a high capacity to store thermal energy, leading to slower heat dispersion (Sharo et. al., 2022).

Effect of Flux Composition on Specific Heat (C_p)

The specific heat (C_p) is the amount of heat energy necessary to raise the temperature of one gram of a substance by one degree Celsius. Specific heat was found to vary between 0.398 to 0.934 J/gK with the variation in flux composition. Trace plot of specific heat is shown in Figure 5.6 (e). An increase in calcite has an increasing effect on the specific heat, whereas an increase in witherite has a decreasing effect. An increase in alumina content in the flux shows a mildly reducing effect on specific heat. The influence of alumina on specific heat is comparatively lower than that of witherite. An increase in fluorspar leads to a slight increase and then a decrease in specific heat. The binary interaction between CaF_2 .BaO has a positive effect, whereas the interaction between CaO. BaO, and Al_2O_3 . BaO has negative effect on specific heat. During welding, electrode filler rod with coating flux gets heated due to resistive heating, this heat is transferred to the coating fluxes.

Coating fluxes with lower specific heat capacity absorb less energy before their temperature rises, allowing them to heat up and respond more quickly during welding. This rapid thermal response helps in softening or disintegrating the flux layer efficiently, facilitating easier detachment and improved slag removal. Since thermal diffusivity is inversely proportional to specific heat, a lower specific heat leads to higher diffusivity, enabling faster heat propagation through the material. Furthermore, thermal diffusivity is also influenced by thermal conductivity – materials with high conductivity and low specific heat exhibit higher diffusivity. Thus, specific heat, diffusivity, and conductivity are interrelated and collectively impact the thermal behavior of flux coatings.

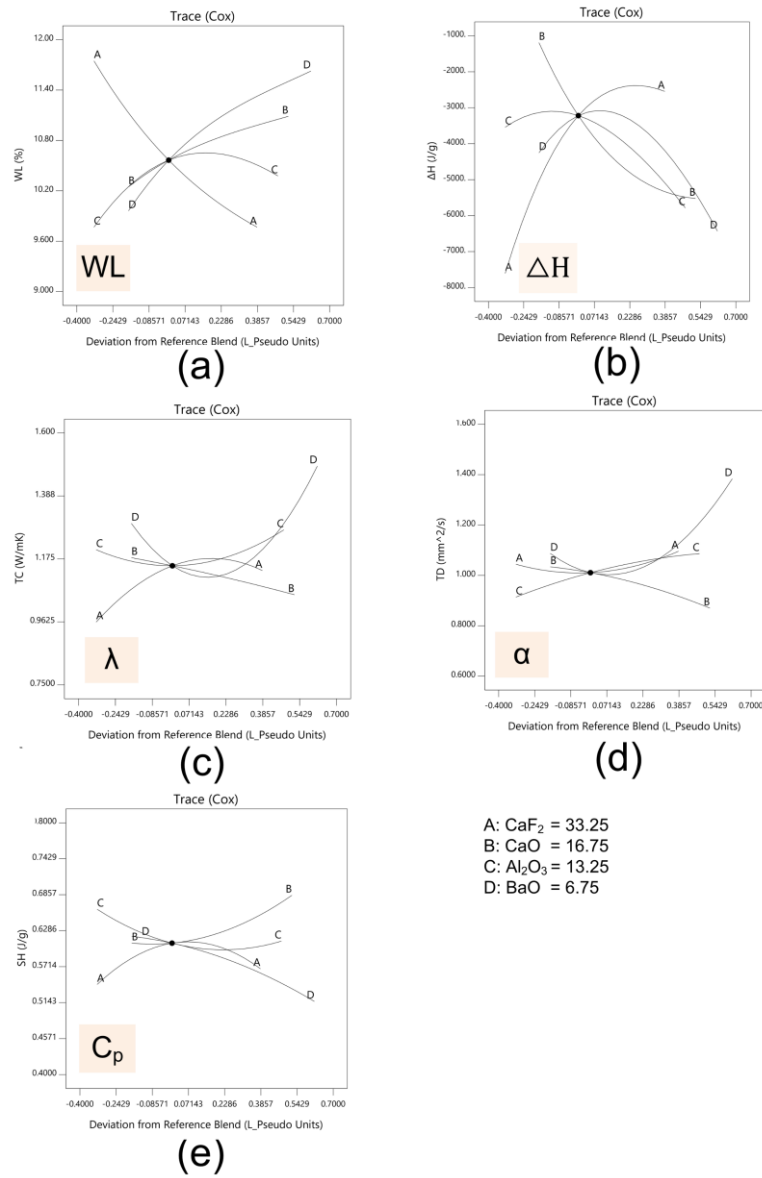


Figure 5.6: Trace plots of the regression model (a) WL, (b) ΔH , (c) λ , (d) α , (e) C_p

The contour plots of the models are displayed in Figure 5.7. The deviation of the responses is shown using contour plots in ternary coordinate. Each group of colors stands for a different response value.

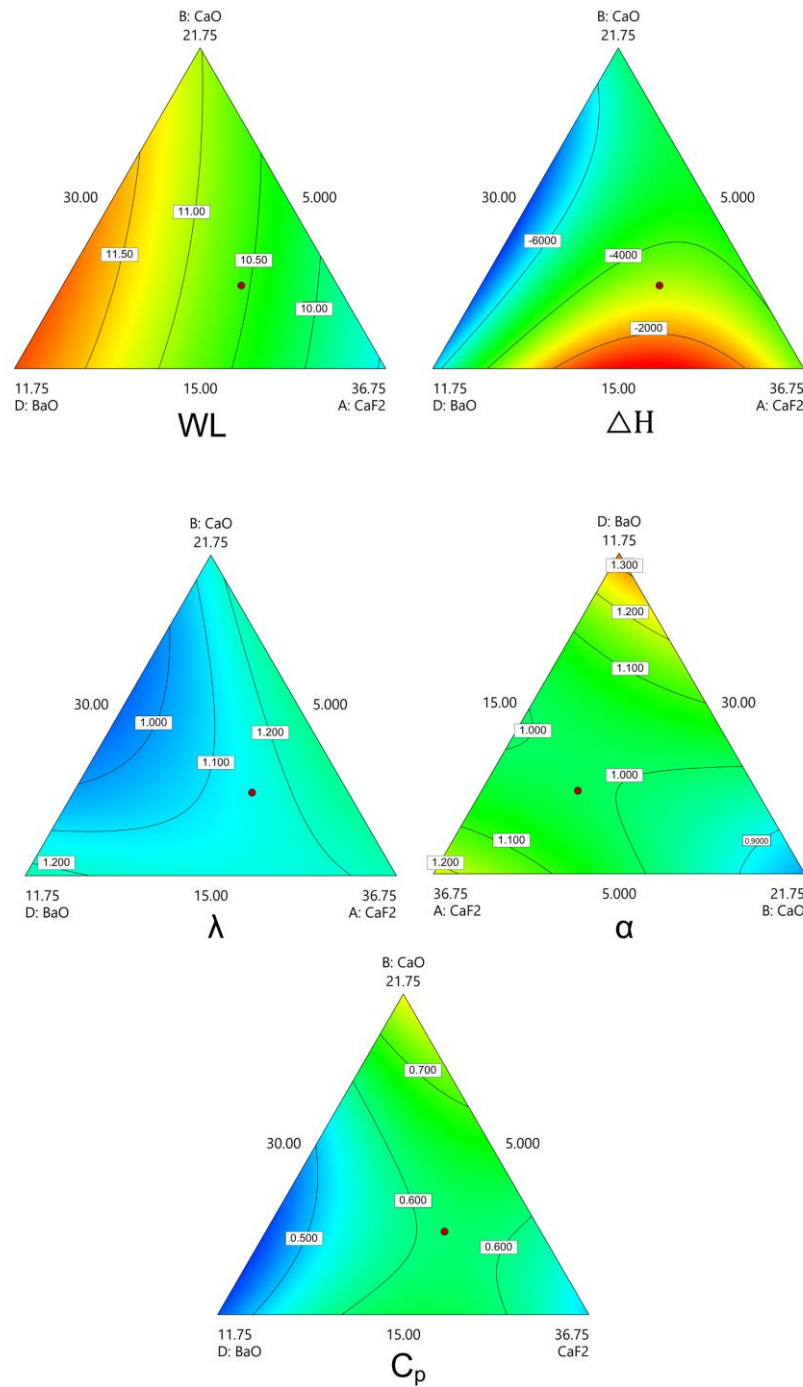


Figure 5.7: Contour plots of the regression model WL, ΔH , λ , α , C_p

5.1.3 Bead-on-plate experiments

(a) Regression analysis of the element transfer and microhardness properties

The Table 5.10, 5.11 shows the element transfer δNi , δMo , δMn and MH results of both the flux systems. The regression models and ANOVA tables are given the appendix Table A9-A12. The models' F-values and P-values have a high signal-to-noise ratio and statistical significance, making them suitable for prediction.

Table 5.10: Estimation of element transfer and microhardness (AF flux)

Bead No.	Ni%	Mo%	Mn%	δNi	δMo	δMn	MH
A1	0.661	0.216	0.925	-0.349	-0.041	-0.175	258.4

A2	0.790	0.221	0.990	-0.220	-0.036	-0.110	257.3
A3	0.705	0.220	1.010	-0.305	-0.037	-0.090	235.9
A4	0.844	0.195	0.884	-0.166	-0.062	-0.216	235.4
A5	0.919	0.198	0.934	-0.091	-0.059	-0.167	246.0
A6	0.832	0.205	1.000	-0.178	-0.052	-0.100	255.8
A7	0.775	0.200	0.952	-0.235	-0.057	-0.148	249.4
A8	0.897	0.206	1.050	-0.113	-0.051	-0.050	246.4
A9	0.827	0.211	0.950	-0.183	-0.046	-0.150	241.3
A10	0.809	0.217	0.867	-0.201	-0.040	-0.233	223.8
A11	0.765	0.202	0.956	-0.245	-0.055	-0.144	242.4
A12	0.810	0.212	1.178	-0.200	-0.045	0.078	259.5
A13	0.758	0.212	0.976	-0.252	-0.045	-0.124	235.4
A14	0.779	0.227	1.030	-0.231	-0.030	-0.070	245.9
A15	0.729	0.213	1.090	-0.281	-0.044	-0.010	250.8
A16	0.925	0.224	1.080	-0.085	-0.033	-0.020	253.4
A17	0.901	0.235	1.100	-0.109	-0.022	0.000	246.7
A18	0.793	0.225	0.995	-0.217	-0.032	-0.105	231.9
A19	0.880	0.217	0.958	-0.130	-0.040	-0.142	259.8
A20	0.811	0.219	0.909	-0.199	-0.038	-0.191	230.8
A21	0.830	0.214	1.010	-0.180	-0.043	-0.090	244.4
A22	0.895	0.204	1.070	-0.115	-0.053	-0.030	255.2
A23	0.753	0.212	0.956	-0.257	-0.045	-0.144	235.7
A24	0.868	0.230	1.010	-0.142	-0.027	-0.090	259.0
A25	0.729	0.208	0.926	-0.281	-0.049	-0.174	242.0
A26	0.899	0.217	1.050	-0.111	-0.040	-0.050	267.2
A27	0.936	0.211	0.940	-0.074	-0.046	-0.160	226.3

Table 5.11: Estimation of element transfer and microhardness (SF flux)

Bead No.	Ni%	Mo%	Mn%	δ Ni	δ Mo	δ Mn	MH
S1	0.770	0.221	1.110	-0.240	-0.036	0.010	256.0
S2	0.901	0.208	1.190	-0.109	-0.049	0.090	245.4
S3	0.798	0.213	0.890	-0.212	-0.044	-0.210	248.4
S4	0.711	0.207	0.980	-0.299	-0.050	-0.120	240.6
S5	0.738	0.205	1.100	-0.272	-0.052	0.000	280.4
S6	0.660	0.211	0.897	-0.350	-0.046	-0.203	230.5
S7	0.815	0.217	0.996	-0.195	-0.040	-0.104	240.6
S8	0.811	0.218	0.938	-0.199	-0.039	-0.162	239.5
S9	0.720	0.210	0.946	-0.290	-0.047	-0.154	266.7
S10	0.860	0.216	0.833	-0.150	-0.041	-0.267	269.0
S11	0.807	0.206	1.050	-0.203	-0.051	-0.050	268.6
S12	0.792	0.215	0.969	-0.218	-0.042	-0.131	237.9
S13	0.857	0.208	1.000	-0.153	-0.049	-0.100	242.1
S14	0.808	0.212	0.836	-0.202	-0.045	-0.264	250.0
S15	0.895	0.211	0.998	-0.115	-0.046	-0.102	275.0
S16	0.787	0.218	1.000	-0.223	-0.039	-0.100	281.9
S17	0.809	0.211	0.896	-0.201	-0.046	-0.204	250.6
S18	0.920	0.217	0.704	-0.090	-0.04	-0.396	270.0
S19	0.782	0.232	1.080	-0.228	-0.025	-0.020	278.1

S20	0.831	0.221	0.852	-0.179	-0.036	-0.248	265.6
S21	0.953	0.212	0.730	-0.057	-0.045	-0.370	267.1
S22	0.816	0.217	1.000	-0.194	-0.04	-0.100	270.0
S23	0.707	0.208	0.993	-0.303	-0.049	-0.107	264.2
S24	0.794	0.217	0.781	-0.216	-0.040	-0.319	244.1
S25	0.841	0.209	0.880	-0.169	-0.048	-0.220	252.9
S26	0.848	0.204	0.860	-0.162	-0.053	-0.240	251.6
S27	0.786	0.212	1.000	-0.224	-0.045	-0.100	272.2

(b) Statistical comparison of regression and ANN models of element transfer and microhardness

Table 5.12 displays the ANN model's training details. A significant positive coefficient of correlation was obtained. In addition, there has been a considerable improvement in RMSE. Figure 5.8 shows the comparison of RA and ANN predictions. The percentage improvement using the ANN δNi model is 44.75% as compared to regression. Similarly, 11% improvement was achieved for δMo prediction, 16.3% for δMn prediction, and 37.96% improvement was achieved for MH prediction. Table 5.13 shows the comparison of ANN and regression prediction on the unseen test data.

Table 5.12: ANN training details for element transfer and MH models

Model	N_H	MSE Training	MSE Validation	MSE_{ANN}	R-value Training	R-value Validation	R-value All
δNi	8	0.0006	0.0012	0.00073	0.94	0.81	0.92
δMo	9	0.000023	0.000068	0.000032	0.82	0.85	0.81
δMn	7	0.0015	0.0021	0.0016	0.84	0.69	0.83
MH	5	17.30	36.08	20.80	0.92	0.88	0.91

Table 5.13: Mean absolute percentage error (MAPE) of RA and ANN prediction on the test data set

#	Actual value	RA prediction	ANN prediction	MAPE_{RA}	MAPE_{ANN}
δNi	-0.200	-0.2433	-0.215	23.37	13.89
	-0.208	-0.2271	-0.240		
	-0.310	-0.1883	-0.251		
δMo	-0.051	-0.0434	-0.047	15.94	9.53
	-0.053	-0.0419	-0.042		
	-0.046	-0.0405	-0.045		
δMn	-0.161	-0.1682	-0.150	30.92	12.39
	-0.100	-0.0620	-0.122		
	-0.090	-0.1353	-0.082		
MH	238.7	249.2	232.7	6.46	2.06
	244.9	255.6	239.5		
	261.3	233.5	265.0		

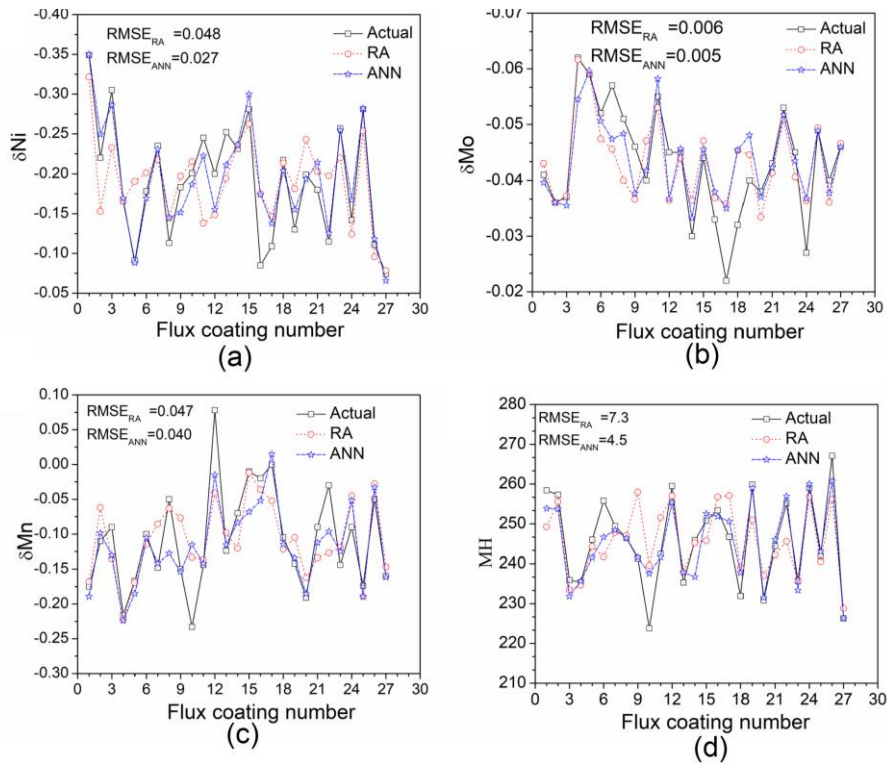


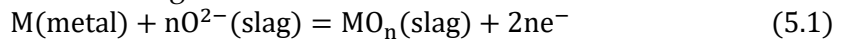
Figure 5.8: Comparison of ANN and regression prediction on unseen test data (a) δNi , (b) δMo , (c) δMn , (d) MH

(c) Effect of flux compositions on element transfer and microhardness

Effect of flux compositions on nickel transfer

The flux has resulted in a variation of 0.661 to 0.936 in the weld, whereas expected weight percentage of nickel was 1.01. loss of alloying element δNi is -0.349 to -0.074 . The weld specimens A5 (-0.091), A16 (-0.085), and A27 (-0.074) have shown highest δNi using the corresponding flux composition, whereas weld specimens A1 (-0.349), and A3 (-0.304) have shown the lowest δNi . Figure 5.9 (a) shows the trace plot, which shows the effect of flux variation from the reference blend on the response (δNi). An increase in BaO has a strong increasing effect on δNi , a comparatively lower but significant increasing effect on δNi was observed with the increase in Al_2O_3 . An increase in CaO has a mostly decreasing effect; slight increase in δNi was observed with high CaO . The binary interaction of $\text{CaF}_2\text{-CaO}$, and $\text{CaF}_2\text{-BaO}$ has resulted in a negative influence on δNi .

The impact of electrochemical processes on the chemical composition of weld metal in direct current (DC) welding is a crucial factor to be taken into account. Electrochemical phenomena may manifest at the interfaces between the slag and the weld pool at elevated temperatures, as well as at the molten electrode tip. The present study employed direct current electrode positive polarity. The determination of the relevance of these effects, which could potentially exert a major impact on the chemical composition of the weld metal, relies on the relative proportions of ions and electrons that are present within the slag. The comprehension of electrochemical reactions is greatly facilitated by the interaction between liquid slag and molten metal contacts. The potential anodic reactions involve the oxidation of alloys and the discharge and absorption of oxygen anions from the slag.



The symbol "M" denotes the alloy element that is found either at the electrode tip/slag or the weld pool/slag interface. Hence, it is expected that there will be considerable oxidation losses of alloy constituents and the uptake of oxygen at the anode (Kim et al., 1990).

Effect of flux compositions on molybdenum transfer

The variation of δMo was -0.062 to -0.022 . The trace plot is shown in Figure 5.9 (b). The increase of fluor spar (CaF_2) present in the flux has a significant positive influence on the molybdenum. An increase in CaO and Al_2O_3 has shown a decreasing effect on δMo . The BaO present in lower amount decreases δMo , whereas a slightly increasing effect was observed on δMo with higher BaO . The binary interaction of $\text{CaO}.\text{Al}_2\text{O}_3$, $\text{CaO}.\text{BaO}$, and $\text{Al}_2\text{O}_3.\text{BaO}$ has increasing effect on δMo ; these interactions were found to produce a synergetic effect on the response. The ternary interaction of $\text{CaO}.\text{Al}_2\text{O}_3.\text{BaO}$ shows a decreasing effect. The weld specimens A4 (-0.062), A5 (-0.059), and A7 (-0.057) have the lowest δMo , whereas weld A14 (-0.03), A24 (-0.027) and A17 (-0.022) have the maximum δMo . Considering there is no other source of molybdenum transfer other than the electrode rod, all weld specimens have revealed negative δMo .

Effect of flux compositions on manganese transfer

The flux variation has influenced the manganese transfer (δMn) from -0.233 to 0.078 . It can be seen that the δMn has a positive value, which suggests that the alloy transfer from slag to weld has occurred. The positive δMn was observed due to the synergetic effect of slag composition and ferromanganese. The trace plot shown in Figure 5.9 (c) shows that the increase in CaF_2 has increasing effect on the manganese transfer. The individual increase of Al_2O_3 , CaO , and BaO has shown a reducing effect on manganese transfer. The ternary interaction of $\text{CaF}_2.\text{CaO}.\text{BaO}$ has an increasing effect on δMn . The δMn for specimens A3 (-0.09) and A13 (-0.0124) is high, whereas the δMn for specimens A9 (-0.15) and A25 (-0.174) is low. The ratio of $\text{CaO}/\text{Al}_2\text{O}_3$ for A3 is 0.9 and for A13 is 0.8 , whereas for specimens A9 it is 1.7 and for specimens A25 it is 2.5 . It can be observed that the loss of manganese content is associated with the rise in $\text{CaO}/\text{Al}_2\text{O}_3$. The findings are in good agreement that the loss of manganese occurs with the gain in oxygen in the weld (Kanjilal et al., 2006). The addition of calcium oxide has been seen to hinder the presence of manganese oxide (MnO) and enhance the transfer of manganese during the welding process. The presence of oxygen during the welding process has an impact on the transfer of Mn content. According to earlier work, manganese loss can and manganese gain can be expressed as:



where, (MnO) is dissolved in slag, $[\text{Mn}]$, $[\text{Si}]$, and $[\text{O}]$ are dissolved in steel

In this work, the electrode rod and ferromanganese are the sources of manganese. The interaction of slag metals leads to the loss or gain of an alloying element. The specimens A15 (-0.01), A17 (0), and A12 (0.078) have shown maximum δMn . The specimens A10 (-0.233), A4 (-0.216), and A20 (-0.191) have shown minimum δMn . The slag developed during welding basically contains ions of Ca^{2+} , Mn^{2+} , Ba^{2+} , Fe^{2+} and O^{2-} , molecules of Al_2O_3 , SiO_2 , and complex networks of aluminate and silicates. Each cation and anion actively participate in the process of building complex molecules through the formation of ion pairs, such as $(\text{Me}^{2+} + \text{O}^{2-})$. The manganese reduction reaction involves the participation of Al_2O_3 and SiO_2 . When present in oxidizing slags, Al_2O_3 and SiO_2 can create four stable products in the reduction process, viz., MnO , $\text{MnO}.\text{SiO}_2$, $2\text{MnO}.\text{SiO}_2$, and $\text{MnO}.\text{Al}_2\text{O}_3$ (Duan et al., 2017). The investigation by Hong et al. show the effect of $\text{CaO}/\text{Al}_2\text{O}_3$ ratio on inclusion formation. When the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is less than 1.5 , the initial activity of CaO in the slag is comparatively low and the activity of Al_2O_3 is relatively high. Ca is introduced into steel at a $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of 1.5 to 2.5 . When the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio reaches 2.5 and above, the activity of Al_2O_3 decreases and the activity of CaO increases. The study concludes that the activity of CaO and Al_2O_3 has a large influence on inclusion formation, and their ratio should be between 1.5 to 2.5 to limit the development of harmful inclusions (Shin et al., 2018). In the present study, the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is between 0.833 and 2.5 .

Effect of flux compositions on microhardness

Figure 5.9 (d) suggests that the increase in CaF_2 increases the microhardness. The individual increase of Al_2O_3 , CaO , and BaO in the mixture resulted in a decrease in microhardness. The microhardness value was found to increase with the binary interaction of $\text{Al}_2\text{O}_3.\text{BaO}$. This

interaction was synergetic in nature. The variation of flux composition has given a variation of microhardness from 223.8 to 267.2 HV. The weld specimens A10 (223.8 HV), A27 (226.3 HV), A20 (230.8 HV) have the least microhardness. The maximum microhardness was obtained for the specimens, viz., A12 (259.5 HV), A19 (259.8 HV), and A26 (267.2 HV). A weak positive correlation coefficient of 0.31 was obtained between BI and microhardness, which suggests BI has a positive influence on microhardness.

The microhardness of a weld is influenced by its microstructure, particularly the distribution and proportion of polygonal ferrite (PF) and acicular ferrite (AF). PF, characterized by larger grains and fewer grain boundaries, offers less resistance to dislocation motion during plastic deformation, enhancing ductility and crack resistance but reducing strength and microhardness. In contrast, AF forms along austenite grain boundaries with a finer structure, increasing grain boundary density, which hinders dislocation movement. This results in higher microhardness and strength but lower ductility. The type of SMAW welding flux used plays a crucial role in determining this microstructure which in turn influences the formation and distribution of PF and AF. Therefore, selecting an appropriate flux is essential to tailoring weld microhardness (Yang et.al., 2020).

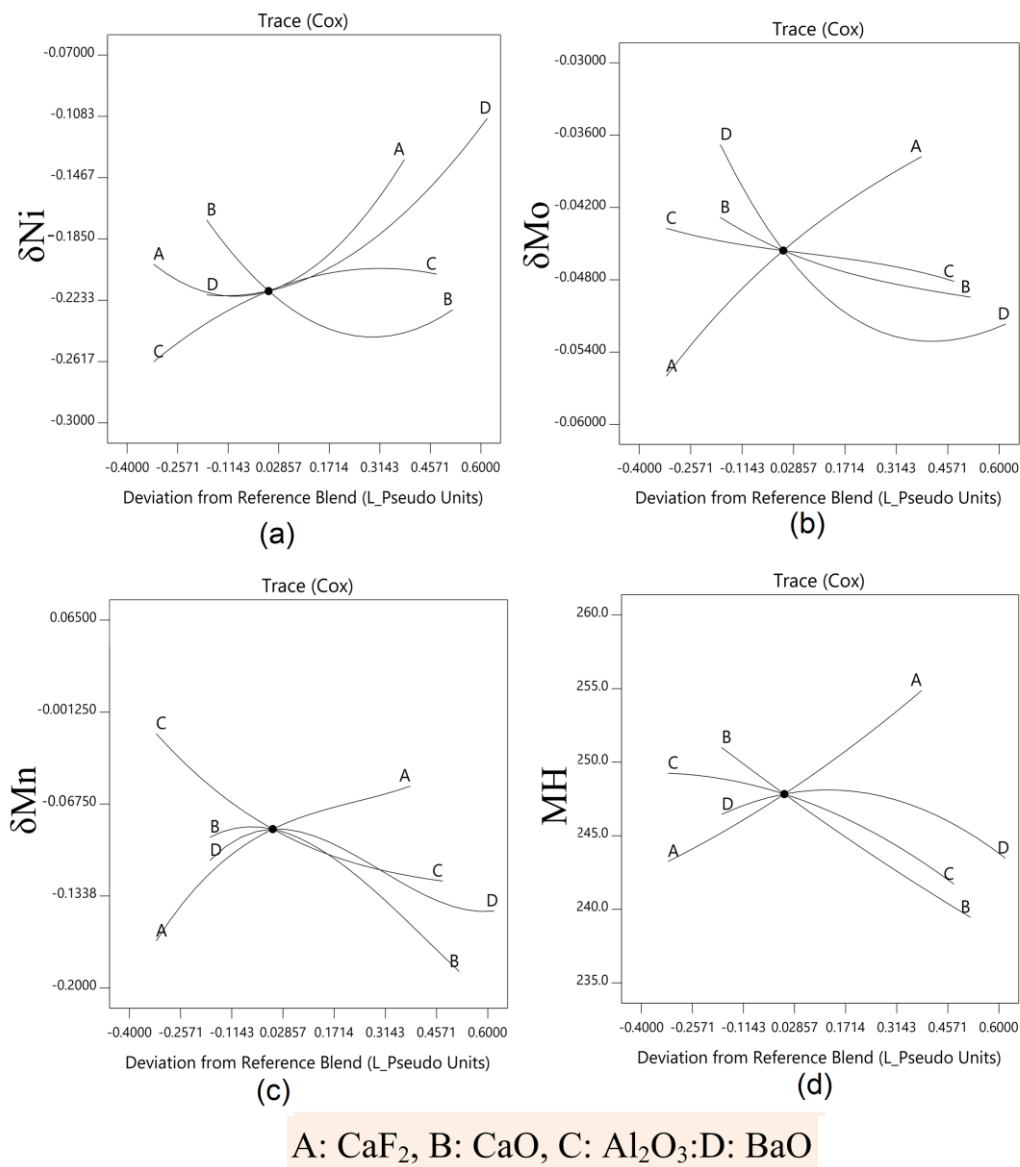


Figure 5.9: Trace plot showing response variation with the deviation from reference blend (CaF₂=33.25, CaO=16.75, Al₂O₃=13.25, and BaO=6.75) (a) δNi , (b) δMo , (c) δMn , (d) MH

Contour plots

The figure presented in this study illustrates the variation in response using a ternary plot, with a constant value of 6.75 for BaO. Each color scheme represents a constant level of response. Figure 5.10 (a) indicates that δNi is negatively affected by the binary interaction of CaF_2 . CaO, and an individual increase in CaF_2 has increasing effect on δNi . Figure 5.10 (b) show that the δMo is positively influenced by the individual increases of CaF_2 , whereas CaO was having reducing effect on δMo . Figure 5.10 (c) depicts that the binary mixture of CaF_2 . CaO with CaF_2 on higher side has increasing effect on the δMo . Figure 5.10 (d) shows that the increase in CaF_2 positively affect the microhardness.

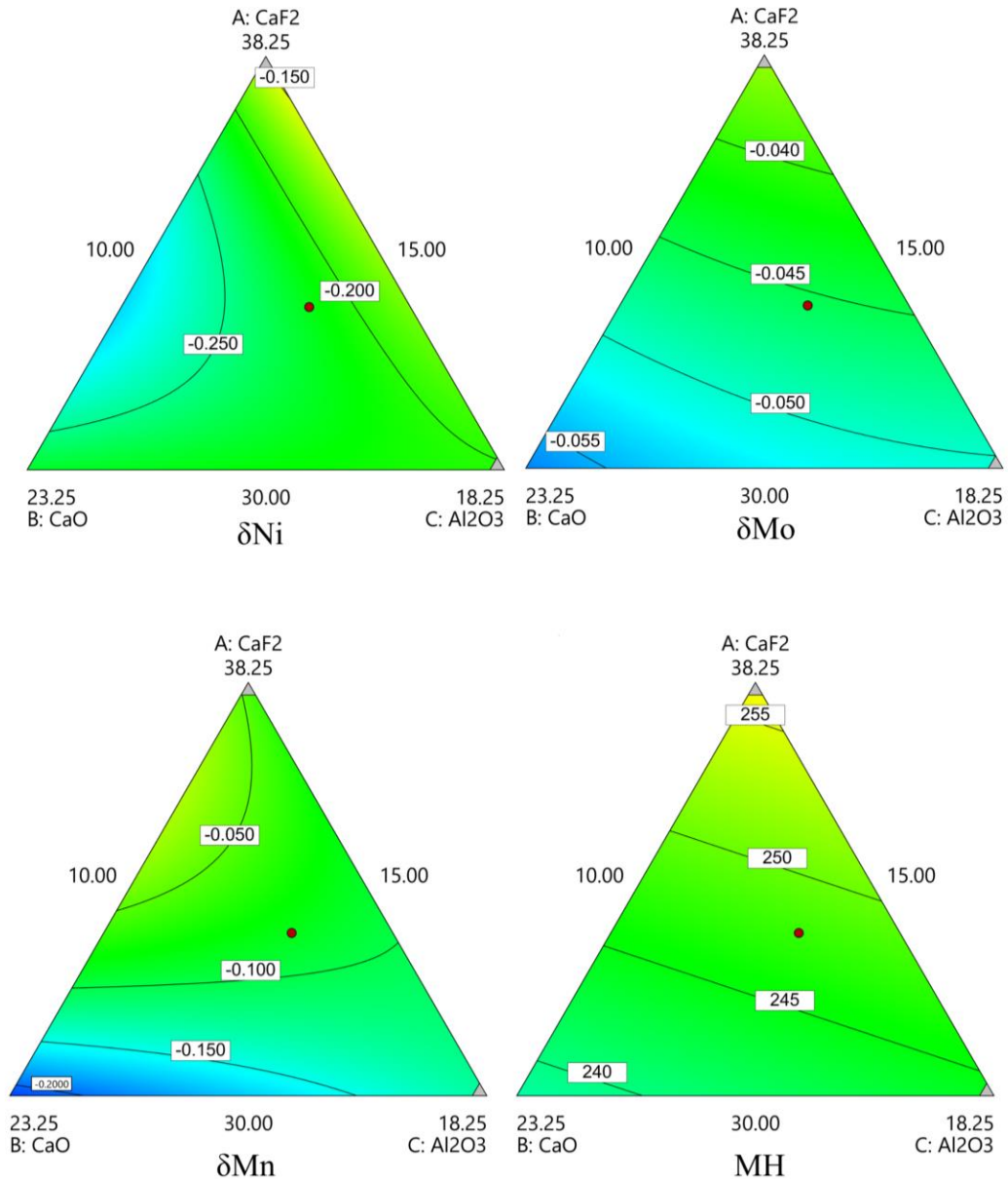


Figure 5.10: Contour plots showing response variation (a) δNi , (b) δMo , (c) δMn , (d) MH

(d) Slag detachability and visual inspection

The visual inspection of the weld bead specimens is shown in Figure 5.11. The weld specimens A6, A9, A24, and A26 have shown a clean and spatter-free weld bead appearance. Spatter development is heavily influenced by the composition and quality of the electrode coating. Spatter reduction is important in SMAW because high spatter is likely to result in post-weld cleanup and potential safety hazards. The weld bead appearance showing a uniform ripple

indicates that the arc was stable. The arc stability in the SMAW process is dependent on the ionization potential, which can vary according to the flux composition. Fluxes with a lower ionization potential tend to provide better arc stability. The weld specimens A6 was produced with a ratio of $\text{CaF}_2:\text{CaO}:\text{Al}_2\text{O}_3::1.45:0.70:0.84$, similarly, A9, A24, and A26 were produced with $\text{CaF}_2:\text{CaO}:\text{Al}_2\text{O}_3$ ratio of 1.75:0.78:0.46, 1.78:0.70:0.52, and 1.75:0.69:0.55 respectively. Except for A6, the ratio of $\text{CaF}_2:\text{CaO}:\text{Al}_2\text{O}_3$ is consistent for good slag detachability. It can be observed that good slag detachability can be attributed to high CaF_2 . Wang et al., concluded that more CaF_2 leads to homogenous porous slag rich in cuspidine and CaF_2 . These slags are relatively strong and have good slag detachability (Wang et al., 2016). Present investigation has also shown that the increase in CaF_2 reduces work of adhesion, increases the wettability contact angle, floatation coefficient, which resulted in reduced slag sticking on steel surface.



Figure 5.11: Visual inspection of bead on plate specimens

(e) *Microstructural studies*

The specimens were selected from the extreme vertices values of the design matrix, hence providing the maximum and minimum flux values for BI. Weld specimens A3 and A13 were welded with coating fluxes AF3 and AF13 respectively; the basicity index of this flux was 2.17. Similarly, specimens A9 and A25 were welded with AF9 and AF25 coating fluxes having a high basicity index (3). The slag-metal inclusion reaction schematic for ultralow carbon steel manufacture was discussed by (Deng et al., 2020); although the current investigation is in welding, the process is analogous. Figure 5.12 (a) depicts the slag-metal inclusion reaction. During welding, inclusion mass transfer occurs between zones R1 and R3, determining the quantity of inclusion in the weld pool. The reduction-oxidation reaction is related to reaction zone R4; multiphase inclusion formation occurs in this zone. Inclusion travels in the slag bulk due to differences in density and buoyant forces. The floatation of inclusion to the slag bulk, R5, is governed by the interfacial forces between slag particles and molten metal, such as work of cohesion and adhesion. The choice of flux composition alters inclusion chemistry, hence changing the interfacial forces between inclusion and molten steel.

Figures 5.12 (b) shows the micrograph of specimens A9 at lower magnification. By examining the micrograph, it is evident that there are several distinct sections present, namely grain boundary ferrite (GBF), acicular ferrite (AF), polygonal ferrite (PF), and widmanstatten ferrite morphology (WM). Welding processes involving fluxes often result in non-metallic inclusion (I) in the weld. With proper control of these inclusions desirable acicular ferrite morphology can be achieved. The micrograph of weld specimens A3, A9, A13, and A25 is shown in Figure 5.12 (c-f). Decomposition of austenite to ferrite begins with the formation of polygonal ferrite (PF) at prior $\gamma-\gamma$ boundaries and proceeds to cover these boundaries, resulting in grain boundary ferrite (Mosallae et al., 2021). The existence of polygonal ferrite has an adverse effect on mechanical characteristics, such as microhardness. The presence of fine ferrite morphology and acicular ferrite is typically associated with enhanced weld performance. Non-metallic

inclusions (NMIs) serve as nucleation sites. The finer structure of ferrite and acicular ferrite is dependent upon the amount of active non-metallic inclusions (NMI). The average microhardness value of specimens A3=235.9 HV and A13=235.4 HV, whereas microhardness for A9=241.3 HV, and for A25=242 HV. There was a mild increase in the microhardness value with the increase in basicity index (2.17 to 3).

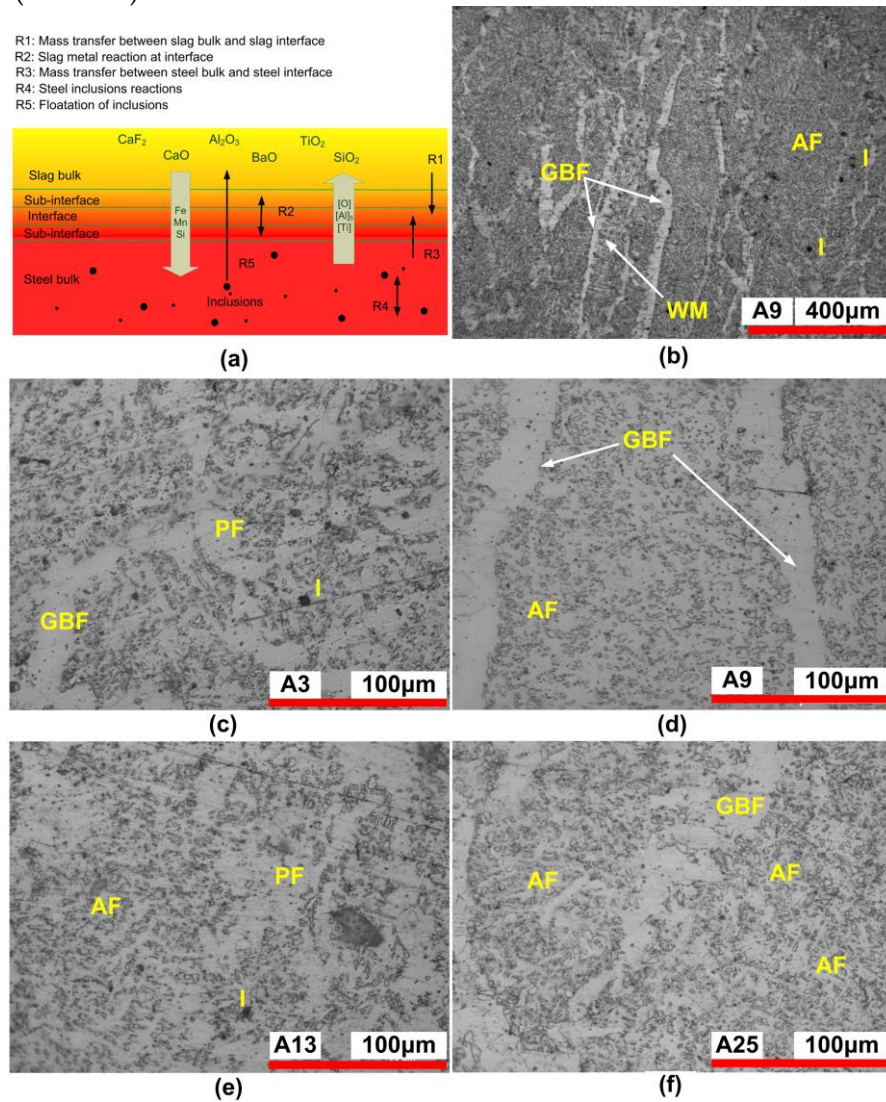


Figure 5.12: (a) Slag metal inclusion reactions (Deng et al., 2020) (b) Microstructure of the weld specimens A9 at low magnification, Microstructure of the weld specimens at high magnification (c) A3, (d) A9, (e) A13, (f) A25.

Figures 5.13 shows EDS and area mapping of specimens A25. EDS shows that inclusion is rich in aluminum and oxygen due to Al_2O_3 , Trace amounts of Mn, Si, Ca, and Ti were also observed (Figure 5.13 (a), (b)). The inclusion rich in Al and O, and weld pool rich in manganese improve the probability for favorable sites of nucleation for AF. Several approaches have been presented in the literature to explain the nucleation of acicular ferrite at inclusions. These mechanisms include a decrease in interfacial energy, which promotes heterogeneous nucleation on the surface of inclusions and epitaxial nucleation on inclusions with high ferrite coherency. In this context, there are two forms of nucleation. The first type is nucleation caused by thermal stresses at the inclusions, which are driven by the differential thermal expansion coefficients of the inclusions and steel matrix. The second type is nucleation, which occurs as a result of solute depletion in the matrix at inclusions (Loder et al., 2017).

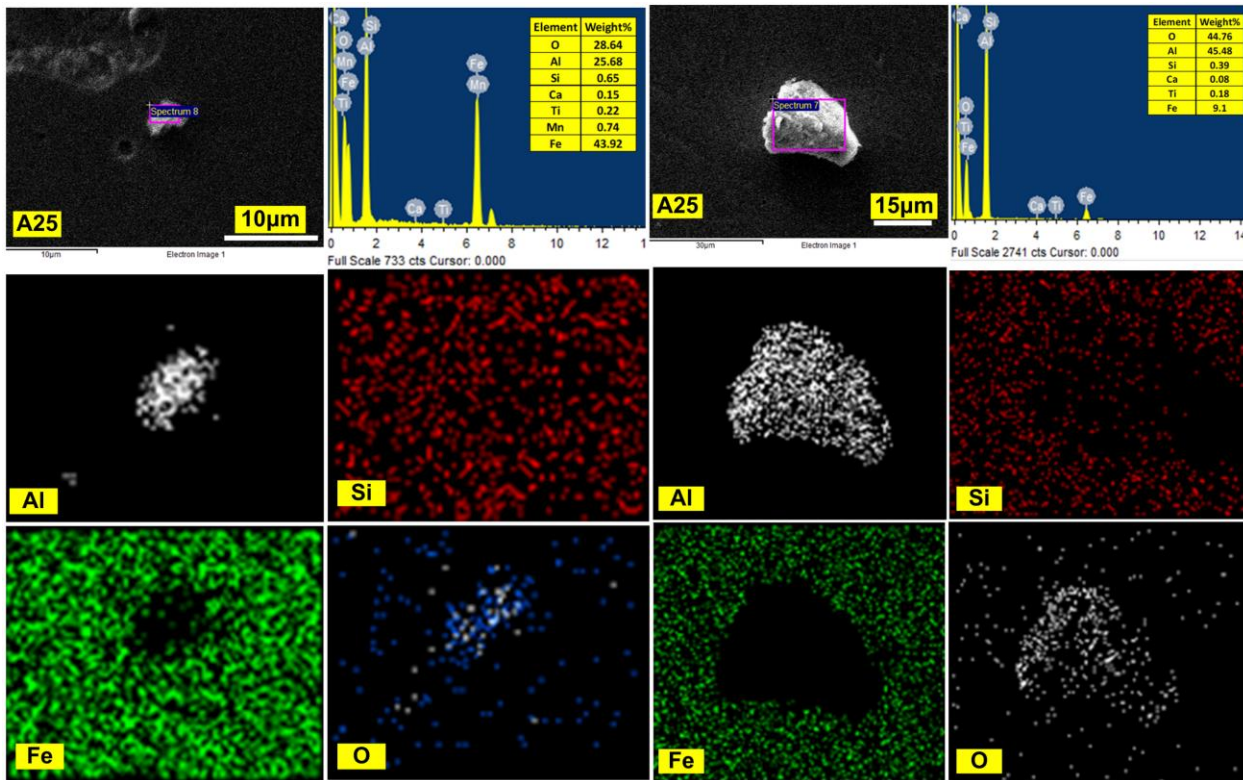


Figure 5.13: EDS and area mapping of specimens A25

During shielded metal arc welding (SMAW), the flux facilitates the transfer of non-metallic inclusions (NMI) to the weld by the interaction between the slag and the metal. The composition of the flux determines the ideal size, type, and quantity of NMI that can be introduced into the weld metal. Bhadeshia and Svensson, together with their colleagues, conducted an experimental and numerical investigation on various weld morphologies that occur in low alloy steel welds, as depicted in Figure 5.14 (Ghomashchi et al., 2015; Bhadeshia et al., 1993). The achievement of a desirable acicular ferrite morphology is contingent upon the presence of an optimal number of non-metallic inclusions (NMI). Non-metallic inclusions that are either excessively large or excessively small do not serve as favorable sites for nucleation. Moreover, when the size of the austenite grain increases, its ability to generate acicular ferrite also increases (Loder et al., 2017).

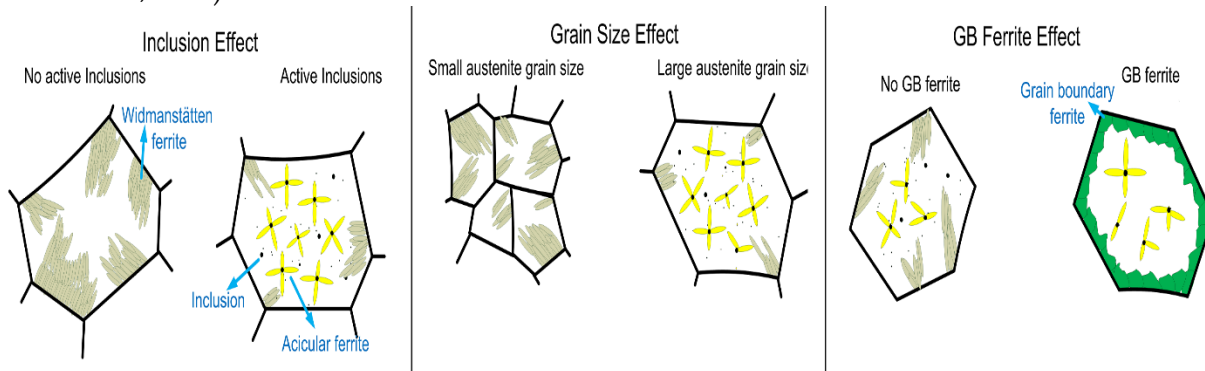


Figure 5.14: Microstructure evolution mechanism in low alloy steel welds (Bhadeshia et al., 1993)

5.1.4 Structural properties of flux and slag

(a) Structural properties of flux

The structural properties of the coating flux are investigated using XRD and FTIR techniques. Figure 5.15 (a) shows the XRD pattern of the flux. The coating flux contains crystalline

mineral powder which can be confirmed by the well-distinguishable peaks of XRD. It can be observed that the peaks have occurred in the same location with slight variations in intensity for different fluxes. XRD results are reasonable since all fluxes have the same constituents with varying compositions. The standard 13 mm dia. pellet with coating flux and KBr was prepared for the FTIR analysis. The FTIR peaks were identified from the previous literature. Figure 5.15 (b) shows a broad transmission peak at 1464 cm^{-1} ($1400\text{ to }1500\text{ cm}^{-1}$) and a sharp peak at 875 cm^{-1} of the internal vibration mode of $[\text{CO}_3]^{2-}$, which has occurred due to the presence of CaCO_3 and BaCO_3 (Chen et al., 2014). Transmission bands of $600\text{ to }800\text{ cm}^{-1}$ can be observed this can be present due to $\text{Al}-\text{O}$ bond in Al_2O_3 (Wang et al., 2006). The spectra show $\text{Si}-\text{O}$ stretching and bending vibrations between $1200\text{--}800\text{ cm}^{-1}$ and $600\text{--}400\text{ cm}^{-1}$ which are characteristics of silicates. The intertetrahedral bridging bonds $\text{Si}-\text{O}-\text{Si}$ in the quartz can be observed at $798\text{--}780\text{ cm}^{-1}$ (Chen et al., 2014). The peak observed at 600 cm^{-1} may be due to $\text{Ti}-\text{O}-\text{Ti}$ stretching (Wang et al., 2006).

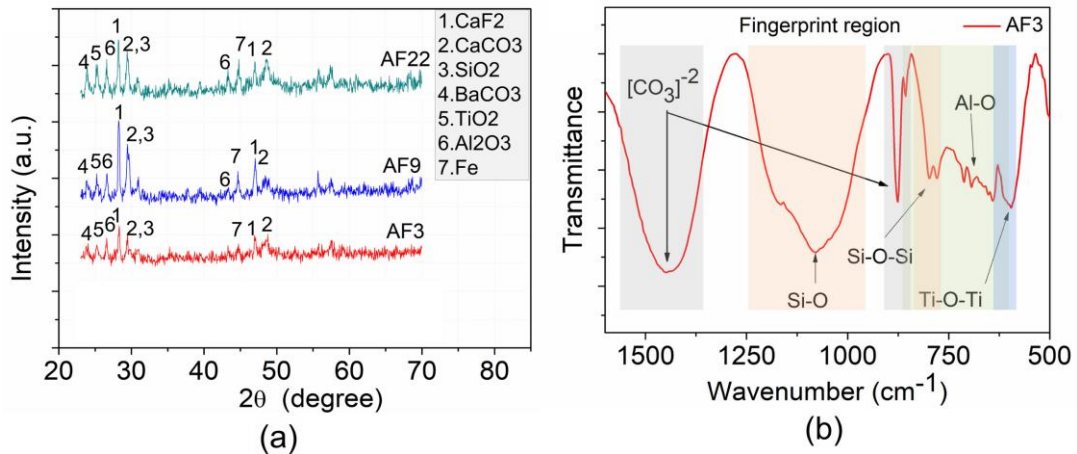


Figure 5.15: (a) XRD pattern of AF flux (b) FTIR spectra of AF flux

(b) Structural properties of quenched slag

The structural analysis of the melts is usually done on the quenched slag. The molten slag was rapidly quenched in the cold water. The XRD diffraction of the quenched slag shows a broad diffusion peak from $20\text{--}40^\circ$ due to its non-crystalline state, although some partial crystallization was also observed (Figure 5.16).

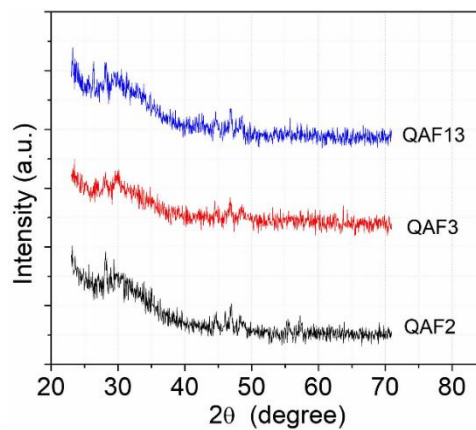


Figure 5.16: XRD pattern of as-quenched slag

The FTIR spectra of the quenched slag is shown in Figure 5.17 (a). The spectra demonstrate three broad transmission bands. The region can be distinguished as $1200\text{ to }800\text{ cm}^{-1}$, and $800\text{ to }550\text{ cm}^{-1}$, and $550\text{ to }400\text{ cm}^{-1}$. The high-frequency region of $1200\text{ to }800\text{ cm}^{-1}$ indicates symmetric stretching vibration of $[\text{SiO}_4]$ – tetrahedral silicate (Zhang et al., 2020).

The stretching vibration in the intermediate region of 800 to 550 cm^{-1} is attributed to the $[\text{AlO}_4]^-$ – tetrahedral units. The slag contains a fixed amount of the SiO_2 , and TiO_2 whereas, Al_2O_3 and other constituents are varied; this leads to a lower content of $[\text{SiO}_4]^-$ – tetrahedral units in the network with varying $[\text{AlO}_4]^-$ – tetrahedral units. The addition of an amphoteric oxide (Al_2O_3) affects the slag polymeric unit. As per the “aluminum avoidance rule” aluminum which is a trivalent ion cannot only produce a tetrahedral structure of $[\text{AlO}_4]^{5-}$, formation of T – O – T (T: Al and Si) linkage structure is more likely due to the charge compensation of network modifying cations. The increase of Al_2O_3 positively influences the viscosity owing to the change in flow unit ($\text{Al} - \text{O} - \text{Al}$, $\text{Al} - \text{O} - \text{Si}$, and $\text{Si} - \text{O} - \text{Si}$) (Choi et al., 2021). The addition of Al_2O_3 with constant SiO_2 favors the formation of $\text{Al} - \text{O} - \text{Si}$ bond compared to other bonds $\text{Al} - \text{O} - \text{Al}$, $\text{Si} - \text{O} - \text{Si}$. Figure 5.17 (a) shows that the formation $\text{Al} - \text{O} - \text{Si}$ is more likely due to the copolymerization $[\text{AlO}_4]^-$ – tetrahedral units and $[\text{SiO}_4]^-$ – tetrahedral units (Wang et al., 2022).

In the fluoride-containing slag (fluoro-aluminate), depolymerization of the network is greatly affected by the F^- anions. The asymmetric vibration of the $[\text{AlO}_n\text{F}_{4-n}]$ ($n = 0 - 4$) tetrahedral complexes are likely to be present in the FTIR spectra. The spectra clearly distinguish $[\text{AlO}_4]^-$ – tetrahedral units. The $[\text{AlO}_6]$ – octahedra and $[\text{AlF}_6]$ – octahedra may also be present at 580 cm^{-1} and 470 cm^{-1} since CaF_2 is present in high concentrations (Park et al., 2002). The equation suggests that the F^- could be a driving force of depolymerization (equation (5.4)).



Although slag has a constant amount of TiO_2 (10%) distinguishable peak has not occurred. It may have an overlap of activity in the intermediate frequency region. Nonetheless, the simpler structure TiO_6 may have modified the network (Kim et al., 2016). The alumino-silicate network is easily distinguishable from its characteristic peaks.

The free oxygen (O^{2-}) breaks the bridged oxygen (O^0) into two non-bridged oxygen (O^-) at high temperatures. The bridged oxygen (O^0) is involved in the complex network structure. The basic oxides (CaO , BaO) are rich in free oxygen (O^{2-}) which leads to the depolymerization process of the network. The depolymerization process can be expressed as:



The acid oxides SiO_2 , Al_2O_3 , and TiO_2 are not rich in free oxygen as compared to basic oxides. The acid oxides such as TiO_2 promote simpler $\text{Ti} - \text{O}$ bonds for TiO_6 octahedral structure than the $\text{Si} - \text{O}$ bond complex network. Inducing simple $\text{Ti} - \text{O}$ network yields more non-bridged oxygen anions (O^-). The interaction of O^- with cations of the substrate by Van der Waals forces occur (Kim et al., 2016).

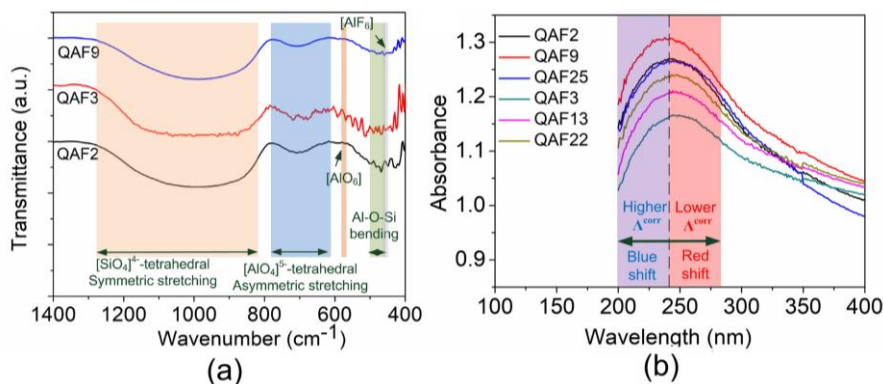


Figure 5.17: (a) FTIR spectra of as-quenched slag (AF) (b) UV-vis spectra of as-quenched slag (AF)

The concept of optical basicity is well utilized by many researchers to correlate the structure with its thermophysical properties. Although (NBO/T) is more suited for correlating the degree of polymerization of the melts over the optical basicity method, mills et al. have suggested corrected optical basicity (Λ^{corr}). The major advantage of using Λ^{corr} is that it also applies to the non-silicate fluxes. The Λ^{corr} provides a global measure of the concentrations of

O^0 , O^- and O^{2-} present in the melt (Mills, 1993). The Λ^{corr} is the measure of the degree of depolymerization. The UV-vis absorption of the as-quenched slag (Figure 5.17 (b)) has shown that the blue shift occurs for the higher basicity slag and a redshift for the lower basicity slag. Table III shows the flux composition of slag, Λ^{corr} , peak wavelength, and peak absorbance in the UV-vis spectra region. So, it can be observed that there is a significant role of corrected optical basicity in correlating the degree of depolymerization in the formulated fluxes.

The FTIR and UV-vis results for the quenched slags of SF flux is given in Figure 5.18 (a) and (b).

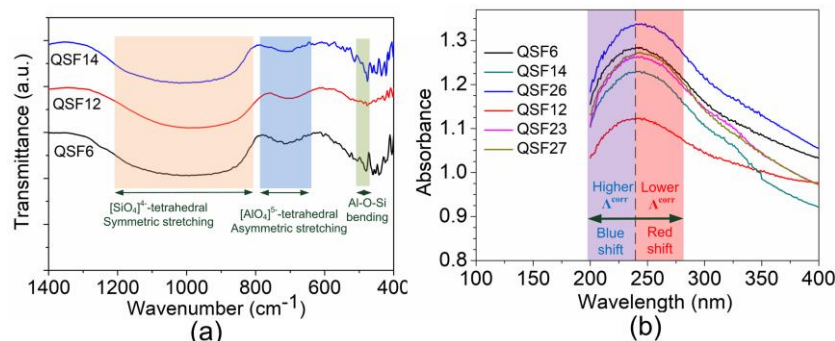


Figure 5.18: (a) FTIR spectra of as-quenched slag (SF) (b) UV-vis spectra of as-quenched slag (SF)

The role of CaF_2 is ambiguous in the literature. The addition of fluorine to the silicate structure causes depolymerization of the network. Divalent calcium ions have electrostatic forces to hold the silicate anions together in pure silicate glasses. The addition of CaF_2 results in the breakage of electrostatic forces and CaF^+ ion pair added to the silicate anions. Figure 5.19 shows the effect of CaF_2 addition on the silicate network. With a higher mole % of CaF_2 , the F^- ion is coordinated with calcium rather than silicon. The addition of CaF_2 with constant CaO/CaF_2 does not participate in the degree of depolymerization (Hayashi et al., 2002).

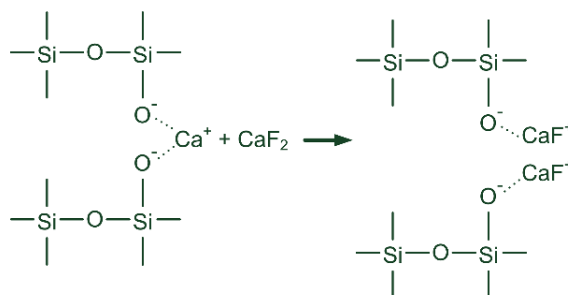


Figure 5.19: Effect of CaF_2 addition to the silicate

5.2 CHARACTERISTICS OF THE SELCTED FLUX FOR WELD

Welding flux helps in transferring the oxygen to the weld metal. The use of flux oxygen potential in welding metallurgy is often utilized to explain how oxygen moves from the slag to the weld metal. The flux characteristics is given in Table 5.14. The basicity index (BI) of the AF and SF flux are 3.34, and 3.42 respectively. The BI of the formulated fluxes is highly basic in nature. The estimation of weight loss (WL %) refers to thermogravimetry (25 – 900°C), AF flux has 5.93 % volatile compounds, whereas SF flux has 10.30 % WL. The AF flux has high CaF_2 which is thermally more stable. The SF flux comparatively has low CaF_2 and high BaO , witherite ($BaCO_3$) is a source of BaO which releases CO_2 on heating. CaO , and BaO both are present in the carbonate form. The fluxes are designed for the low WL %, Lower WL % reduces the gaseous and vapor infiltration in weld pool. BaO is more thermally stable than CaO . The systematic substitution of CaO , with BaO was done to ensure synergistic results. The presence of BaO in the welding flux

improves the acicular ferrite in the weld microstructure, which is responsible for high toughness with high strength (Chang et al., 2008). An increase in strength is often associated with a reduced toughness value, so acicular structure in weld becomes favorable for improving strength and toughness simultaneously. The degree of depolymerization is correlated to Λ^{corr} . The water vapor solubility ($\text{LogC}_{\text{H}_2\text{O}}$) based on Λ^{corr} was calculated, the water vapor capacity is 3.6068 and 3.6076 which is nearly the same. The water vapor solubility of slag has a considerable impact on the amount of hydrogen that the molten weld metal absorbs from the arc. In general, larger slag water capacity reduces hydrogen content in the weld metal. This variation in hydroxyl capability with slag basicity explains how adjusting basicity could decrease hydrogen concentration in the weld metal (Du Plessis et al., 2007). The viscosity was theoretically estimated using Λ_{new} new optical basicity. Although, the BI and Λ^{corr} are nearly the same for both fluxes, Λ_{new} has slight variation which overall results in the variation of viscosity (Yan et al., 2019). Slag viscosity in SMAW has significance for protecting the weld pool, managing the cooling rate, and providing easy slag removal. Optimal viscosity assists in the formation of a stable, protective layer that shields the weld from impurities, promotes consistent weld quality, and allows for a smooth, clean finish.

Table 5.14: Coating flux characteristics used for weld AF_W and SF_W

#	WL %	BI	Λ^{corr}	$\text{LogC}_{\text{H}_2\text{O}}$	Λ_{new}	η (Pa.s)
AF	5.93	3.34	0.8173	3.6068	2.00223	0.137328
SF	10.30	3.42	0.8174	3.6076	2.04417	0.083911

5.3 CHARACTERIZATION OF WELD

The weld AF_W, SF_W were prepared using the developed electrode, whereas CE_W was prepared using commercial E8018-G electrode. The chemical composition of weld and base X70 was analyzed using Asphire AS-S3 OES instrument (Table 5.15). The formula given by Ito-Bessyo was used to calculate the carbon equivalent (P_{cm}) value. API limit for P_{cm} value is (<0.25%).

$$P_{cm} = C + \frac{\text{Si}}{30} + \frac{\text{Mn} + \text{Cu} + \text{Cr}}{20} + \frac{\text{Ni}}{60} + \frac{\text{Mo}}{15} + \frac{\text{V}}{10} + 5B \quad (5.6)$$

Table 5.15: Chemical composition of weld and X70 base metal

#	C	Si	Mn	Al	Ti	Mo	Ni	Cu	V	Nb	P+S	P_{cm}
X70	.037	.290	1.690	0.01	0.09	.028	0.402	0.020	.048	.040	.044	0.145
AF_W	.041	.269	1.507	0.02	0.13	.214	1.259	<.02	.051	.365	.056	0.154
SF_W	.043	.255	1.328	0.01	0.10	.143	1.381	0.121	.046	.246	.051	0.152
CE_W	.029	.275	1.537	<.01	<.02	.132	0.609	<.02	.007	.020	.051	0.129

5.3.1 Inspection of weld

Figure 5.20 (a) shows the prepared welds, all welds have shown low spatter and uniform weld bead. Figure 5.20 (b) and (c) shows the dye penetrant test of the weld. The dye penetration test was performed, the plate was cleaned and red dye was applied for 10 minutes dwell time, after that dye was cleaned and developer was applied. The developer soaks out the red dye in case of any cracks. The welds have shown no signs of cracking which can be attributed to the lower P_{cm} values. The red spots on the welds are start up porosity which can be present during start and end of welding, these are generally grinded off. Figure 5.20 (d) shows the cross sectional specimens cut for metallurgical and microhardness test, it shows no lack of fusion present.

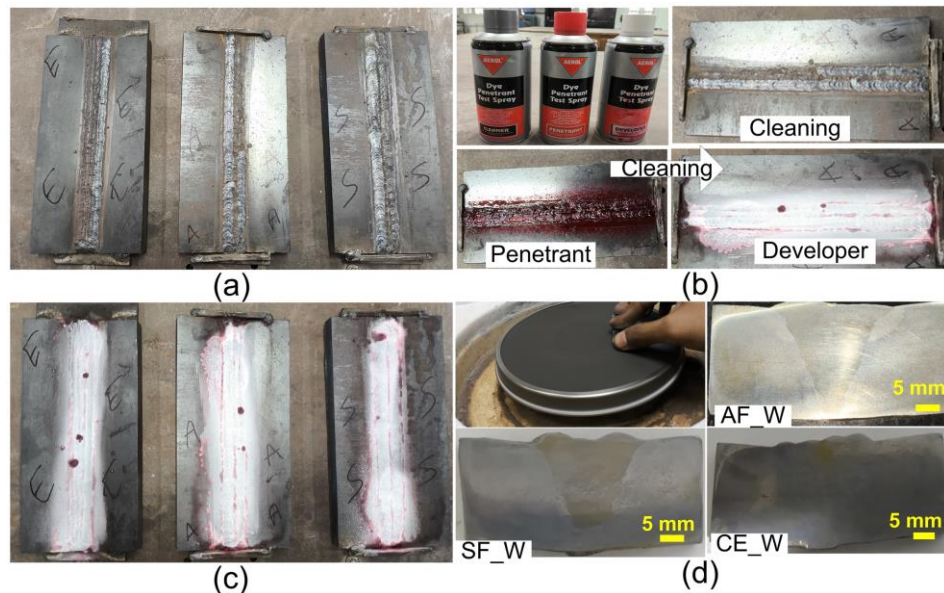


Figure 5.20: (a) Prepared welds, (b) Dye penetrant test, (c) Weld surface with developer (d) Specimens from weld cross section for metallurgical tests

5.3.2 Impact test

The Charpy V-notch test, is critical for evaluating pipelines. Pipeline steels must be able to withstand potential impacts during transportation and operation. This test determines the energy absorbed by a notched specimen when shattered under a standard impact load, providing information on the steel's capacity to withstand fracture. Figure 5.21 shows the impact energy absorbed by the X70 base metal and the weld metal, Figure 5.22 shows the SEM fractography of X70 and the weld metal. The base metal is not broken with the hammer, which shows its excellent impact absorbing capacity. The average impact energy was estimated to be 48.4 J/mm, which was still a conservative value. The weld AF_W has resulted in an average impact energy of 22.13 J/mm the weld SF_W has 19.9 J/mm, and the weld CE_W has 22.99 J/mm. The absorbed energy of AF_W and CE_W is nearly the same and for the SF_W is slightly on the lower side.

The fracture surface of X70 base metal displayed significant plastic deformation, indicating a ductile fracture. Weld metal fractures have mix mode, which can be confirmed from the quasi-cleavage plane (Wang et al., 2019). Furthermore, acicular ferrite is a beneficial weld microstructure due to its capacity to enhance the toughness of the weld metal. As the volume fraction of acicular ferrite increased, the Charpy toughness of the welds improved. The fine, interlocking grains of acicular ferrite offered superior resistance to fracture propagation by cleavage. In contrast, primary ferrite or ferrite with secondary phases reduced weld metal toughness, as these microstructures facilitated more rapid crack propagation. The addition of BaCO_3 was advantageous, as it accelerated the formation of acicular ferrite. As discussed previously, Ni reduces the GBF and results in fine morphology, which is suitable for interlocking grain.

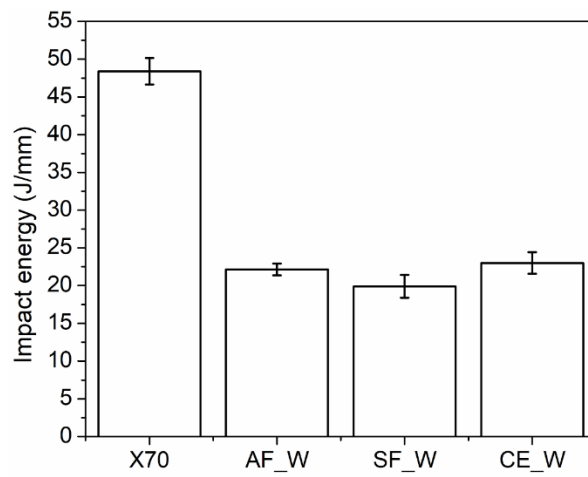


Figure 5.21: Average Charpy impact energy of X70 and weld

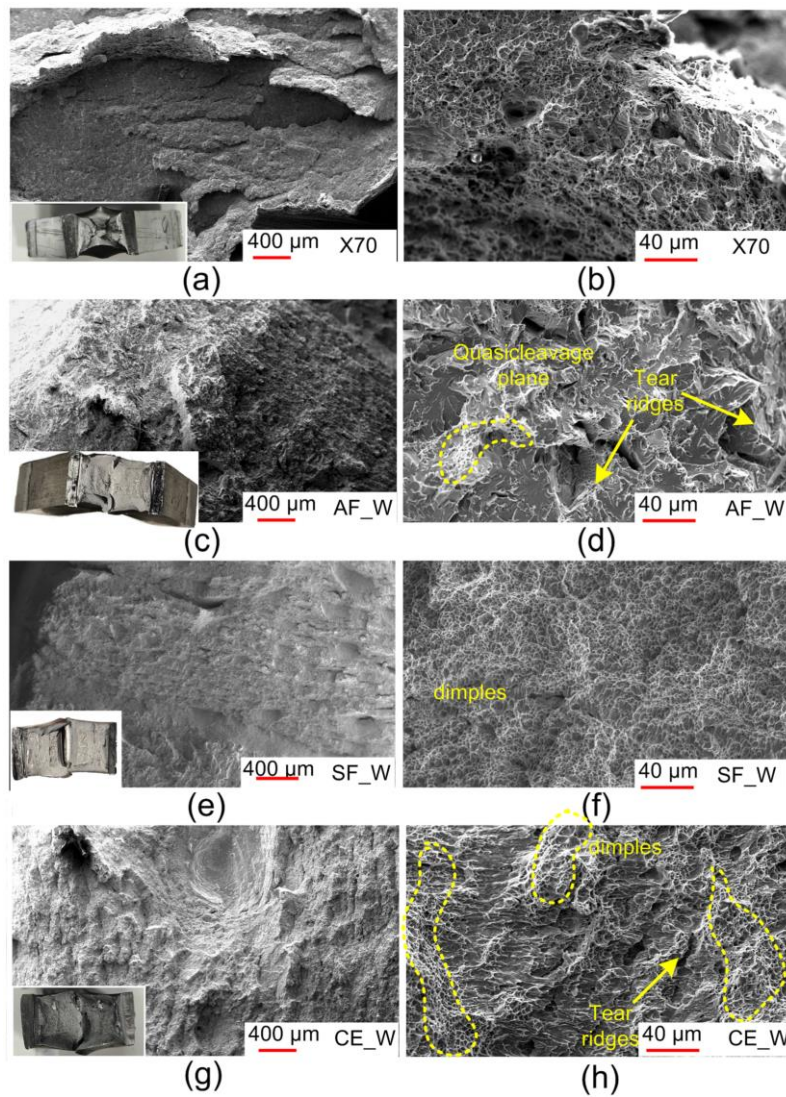


Figure 5.22: SEM fractography of (a, b) X70, (c, d) AF_W, (e, f) SF_W, (g, h) CE_W

5.3.3 Microhardness test

(a) Cap to root pass hardness

The microhardness examination of the welds was performed from cap to root. Figure 5.23 (a) shows the average microhardness of the weld. It can be seen that the microhardness of the AF_W (302.4 ± 19.5 HV) and SF_W (285.8 ± 18.5 HV) is higher than the CE_W (234 ± 19.7 HV). The increase in HV of the weld can be attributed to the, acicular ferrite, thin grain boundary, and martensite austenite. The root weld microhardness is almost similar due to the same electrode used for root pass. The Python code available on GitHub by Nishikawa A. was used to generate phase fraction microhardness vs cooling rate (Hunter, 2007; Li et al., 1998; Nishikawa; Saunders et al., 2004). The chemical composition of the weld was used to generate phase fraction microhardness vs. cooling rate diagrams. Figure 5.23 (b) illustrates a phase fraction microhardness of the welds. It can be seen that the predicted microhardness values are in good agreement with the experimental value. The weld AF_W has higher microhardness than the weld SF_W, even when the rod (ER80S-Ni1) is common. This variation has been imparted due to fluxes; the developed flux has improved the microhardness of the weld. Although the BI , Λ^{corr} are similar, but Λ_{new} value is slightly different, which resulted in variation in the viscosity of the molten slag. Thermogravimetry WL% for the AF flux is lower than the SF flux, low WL% reduces the gaseous infiltration in the weld.

In Figure 5.23(a), the microhardness distribution of CE_W from the cap pass to the root pass shows a gradual increase. Since the root pass is made using the same electrode, the microhardness remains nearly constant across all the welds. This trend is primarily attributed to thermal straining resulting from the successive deposition of filler metal during the multi-pass welding process. Each additional weld pass induces localized thermal cycles, leading to cumulative thermal stresses and strain hardening – particularly in the lower regions of the weld – resulting in higher microhardness at the root compared to the cap (Ganguly et al., 2016). However, this trend was not clearly observed in the AF_W and SF_W welds. Nevertheless, as discussed in the following section, the average cap pass microhardness is lower than that of the fill pass, which aligns with the above explanation.

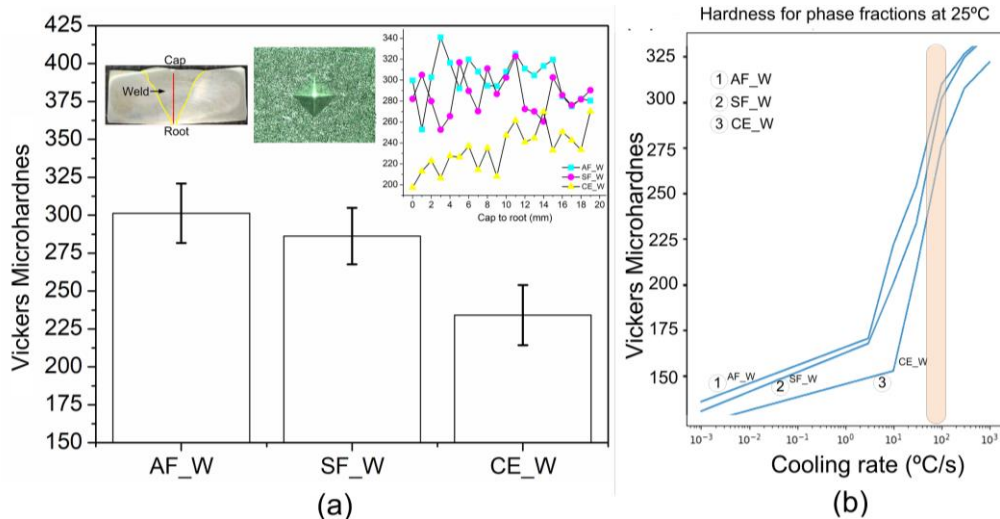


Figure 5.23: (a) Average microhardness of weld from cap to root, (b) Microhardness vs cooling rate prediction from the chemical composition

(b) Weld centerline to HAZ hardness

The microhardness variation from weld centerline to HAZ is shown in Figure 5.24 (a, b). The multi-pass weld bead has a reheated zone, which creates a coarse and fine zone; this results in the variation of the microhardness. The average microhardness in the fill pass section of the AF_W is 331.8 ± 21 HV, for the SF_W it is 301.9 ± 12.6 HV, and for the CE_W it is 223.2 ± 8.7 HV. The HAZ in the fill side has a microhardness 256 ± 8.2 HV. The X70 base has a microhardness of

268.1±9.5 HV. Here, the average microhardness of HAZ and X70 from the fill-pass side of all weld was considered. The microhardness indents were taken nearly 2 mm below the cap surface. The average microhardness in the cap pass section of the AF_W is 290.3±16.7 HV, for the SF_W it is 271.5±23.1 HV, and for the CE_W it is 226.3±15 HV. The HAZ on the cap side has a microhardness 243±9.7 HV. The X70 base has a microhardness of 261.7±9.5 HV. The results obtained can be justified on the basis of the cooling rate observed by different sections of the weldment. The cap pass experiences a slower cooling rate as compared to the reheated zone in the fill pass, so the average microhardness weld from the fill pass is higher than the cap pass. Similarly, the HAZ from the fill pass side has a higher average microhardness value than the cap pass side. The microhardness values of the X70 base metal are nearly the same due to the reduced effect of peak temperature away from the centerline. The standard deviation of the weld microhardness was higher than the HAZ and X70 base due to the thermal cycles experienced by the multi-pass weld bead.

The variation in microhardness profile is resulted due to the reheated weld zones. The increased hardness is attributed to the formation of hard M-A constituents during thermal cycles in multi-pass welding. The regions rich in M-A constituents have higher stress concentrations than those containing acicular ferrite. These hard zones interact with surrounding softer regions, promoting the formation of local brittle zones (Wang et. al., 2017). The cooling rate affects the microstructure and hardness in high-strength low-alloy steels and welds during welding. Rapid thermal cycles during welding, especially in the coarse-grain, significantly alter material properties. The faster cooling decreases the transformation start temperature, increases high-angle grain boundary (HAGB) density, and raises hardness. A Hall-Petch-type relationship links increased hardness to higher HAGB density, emphasizing that grain boundary strengthening through dense high-angle boundaries enhances weld region hardness (Roy et. al., 2022).

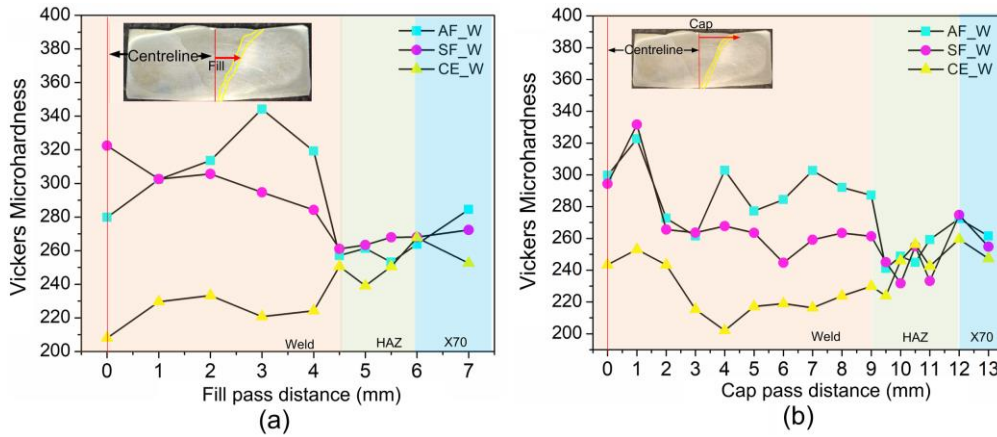


Figure 5.24: Microhardness variation from weld centerline to HAZ (a) Fill pass, (b) Cap pass

The weld strength matching ratio which is a comparison of weld and base metal is shown in equation (5.7). It is considered "overmatch" when the weld strength exceeds the BM strength and "undermatch" when the weld strength is lower than the BM strength (Figure 5.25). HAZ softening ratio and % HAZ softening was calculated from the equation (5.8) and (5.9), respectively (Garcia et al., 2022). The Min hardness of HAZ is 223 HV, the minimum HAZ hardness is influenced by the steel's composition and the thermal cycle (peak temperature and cooling rate) during welding. This minimum hardness value is not standardized and is often reported as the absolute lowest value in the HAZ. The BM X70 hardness is 268 HV, and the weld hardness for AF_W, SF_W, and CE_W, is 302 HV, 285 HV, and 234 HV, respectively.

$$\text{Weld metal strength matching ratio} = \left(\frac{HV_{WM}}{HV_{BM}} \right) \quad (5.7)$$

$$\text{HAZ softening ratio} = \left(\frac{\min HV_{HAZ}}{HV_{BM}} \right) \quad (5.8)$$

$$\% \text{HAZ softening} = \left(\frac{HV_{BM} - \min HV_{HAZ}}{HV_{BM}} \right) \times 100 \quad (5.9)$$

The weld strength matching ratio for AF_W, SF_W, and CE_W weld was 1.12, 1.06, and 0.87 respectively. The HAZ softening ratio is 0.83 and the %HAZ softening is 16.79%.

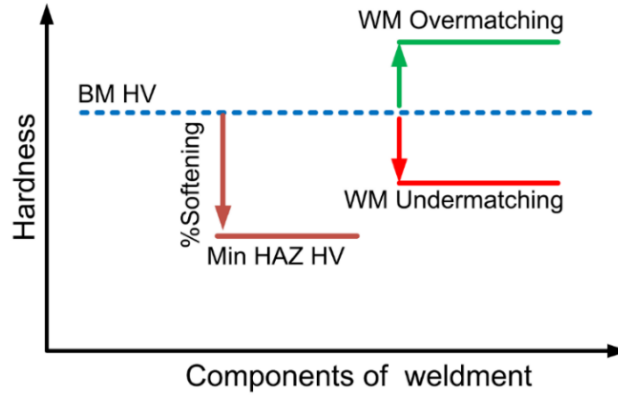


Figure 5.25: Hardness diagram showing BM, HAZ, and weld components, along with terms for strength imbalance (Garcia et al., 2022)

5.3.4 Tensile test

Figure 5.26 (a) shows the engineering stress strain curves from the tensile tests. The yield strength was calculated at 0.2 % offset. The yield strength and ultimate tensile strength of BM X70 was $\sigma_{YS} = 504.87$ MPa, $\sigma_{UTS} = 625.38$ MPa. The minimum yield strength limit for the API X70 is 483 MPa. The yield strength σ_{YS} of the weldment AF_W, SF_W and CE_W was 494.49, 543, and 480.9 MPa respectively. The ultimate tensile strength σ_{UTS} of the weldment AF_W, SF_W and CE_W was 609, 636, and 563.5 MPa respectively. The weld strength mismatch ratio of the weldment AF_W was $\frac{(\sigma_{YS})_{AF_W}}{(\sigma_{YS})_{X70}} = 0.98$, and $\frac{(\sigma_{UTS})_{AF_W}}{(\sigma_{UTS})_{X70}} = 0.97$, the weldment AF_W is close to evenmatched. The weld strength mismatch ratio of the weldment SF_W was $\frac{(\sigma_{YS})_{SF_W}}{(\sigma_{YS})_{X70}} = 1.07$, and $\frac{(\sigma_{UTS})_{SF_W}}{(\sigma_{UTS})_{X70}} = 1.016$, and for CE_W it was $\frac{(\sigma_{YS})_{CE_W}}{(\sigma_{YS})_{X70}} = 0.95$, and $\frac{(\sigma_{UTS})_{CE_W}}{(\sigma_{UTS})_{X70}} = 0.90$. Figure 5.26 (b) shows that the weld failure has occurred in the HAZ region. The elongation % of the X70 tensile test was 31 % and for weldment AF_W, SF_W and CE_W 18 %, 18.5 %, and 20 % respectively.

The yield to ultimate strength ratio also known as Y/T ratio for X70, AF_W, SF_W and CE_W was 0.807, 0.812, 0.854, and 0.853 respectively. The low Y/T ratio is desirable property which indicates its ability to deform plastically. The results suggested that the strength has been increased with comparable impact property. The weld AF_W has shown improved mechanical properties.

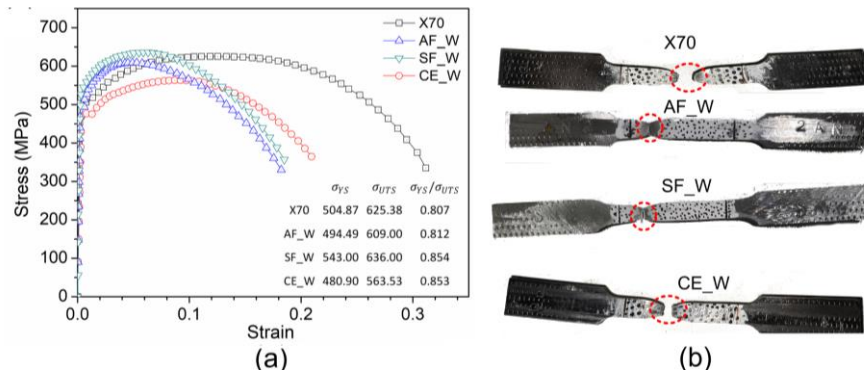


Figure 5.26: (a) Engineering stress-strain curves of X70, AF_W, SF_W, and CE_W (b) Rupture location of tensile specimens

5.3.5 Effect of hydrogen charging

Hydrogen-induced cracking (HIC) and hydrogen embrittlement (HE) are distinct but related phenomena. HIC involves cracking caused by hydrogen gas pressure buildup, typically in HSLA steels under H_2S -rich environments, and leads to irreversible damage. In contrast, HE results from hydrogen atoms within the metal lattice reducing ductility. It affects various metals, often under milder conditions, and is typically reversible upon hydrogen removal. In present work cathodic charging technique was employed to promote H_2S charging. The specimen was immersed in a 0.5 M sulfuric acid+5g/l thiourea solution. A DC power source was used to supply 50 mA/cm² current density for 10 h. The amount of hydrogen charging (PPM) was not estimated, hydrogen embrittlement was compared for all welds with common charging duration. Two tensile test specimens from each weld and base were hydrogen charged. In tensile specimen charging, two faces of gauge length (25 mm) were exposed to solution. Microhardness test with and without charging was also performed.

The cathodic charging technique introduces hydrogen into the metal by applying a negative voltage in an electrolytic cell. The metal specimens is immersed in an electrolyte solution, and the applied current reduces hydrogen ions (H^+) to form hydrogen gas, which diffuses into the metal. The Figure 5.27 (a) show the schematic of hydrogen charging effect; (b) show the macro appearance of the charged specimens; (c) show the SEM micrograph of the charged surface; and cracks appeared on the base metal. The specimens were hydrogen charged for 10 h. Few cracks were visible in the base metal, although no visible cracks were found in the weld. The hydrogen absorbed in the weld and base metal was likely to be insufficient, implying that hydrogen levels were too low to promote a significant number of cracks. Figure 5.28 shows the comparison of the microhardness of the charged and uncharged specimens. The microhardness value difference for with and without charging is small whereas large standard deviation is observed. Although, overall reduction in microhardness is observed for with charging, results might not be considered conclusive enough with ex situ charging. The effect of hydrogen charging on microhardness variation investigated by previous researchers was also reported to be negligible (Bae et al., 2022; Latifi et al., 2017).

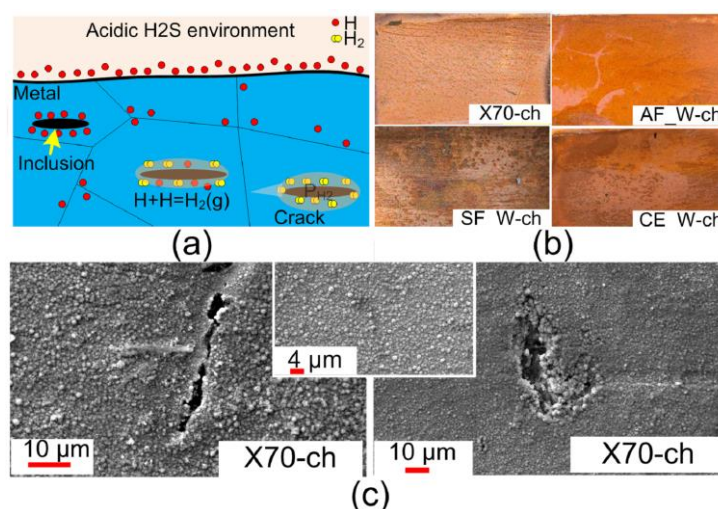


Figure 5.27: (a) Schematic of hydrogen charging, (b) appearance of charged specimens, (c) SEM micrograph of charged X70.

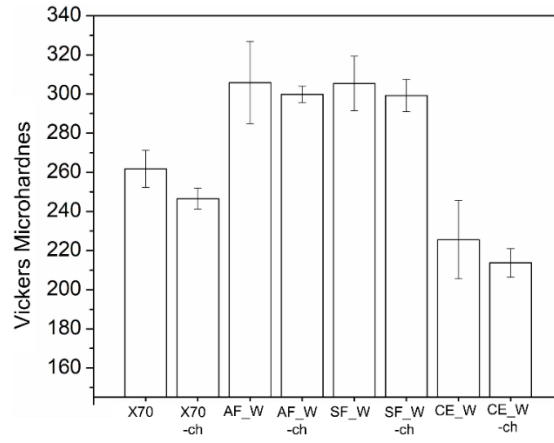


Figure 5.28: Microhardness of with (-ch) and without hydrogen charging of X70, AF_W, SF_W, and CE_W

To examine the effect of hydrogen on the tensile behavior of base and weld metal, cathodic charging of the tensile specimens was carried out. Figure 5.29 shows the tensile stress strain curves of with (-ch) and without hydrogen charged tensile specimens. Ex-situ charging involves a pre-hydrogenated specimens, during which hydrogen gradually diffuses out as the tensile test proceeds. In-situ hydrogen charging leads to the highest susceptibility to embrittlement among different hydrogen environments. In-situ hydrogen charging has become the preferred approach for assessing hydrogen-induced mechanical degradation in BCC steel. This preference is due to the high diffusion coefficient of hydrogen in steel, which causes hydrogen to escape from ex-situ charged specimens under applied stress (Yadav et al., 2023). Although in-situ investigations are preferred, present study has used ex-situ approach due to its ease. Also, the main objective of the test was to compare the weld metal and base metal.

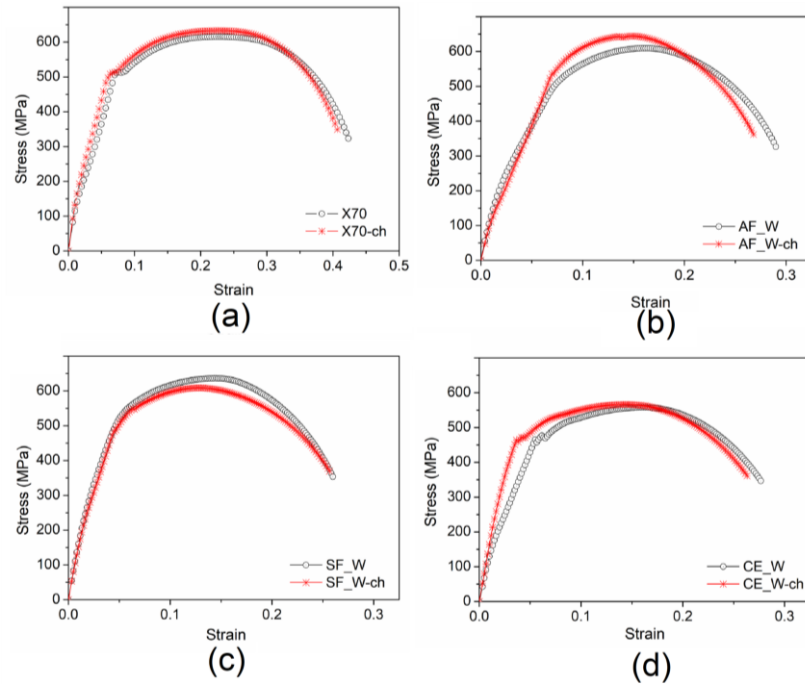


Figure 5.29: (a-d) Tensile stress strain curves of base and weld metal with (-ch) and without hydrogen charging

The loss of ductility due to hydrogen charging was estimated by hydrogen embrittlement index (HEI):

$$\% RA = 100 \times \frac{(A_o - A_f)}{A_o} \quad (5.10)$$

$$HEI = \frac{(RA_{\text{uncharged}} - RA_{\text{charged}})}{RA_{\text{uncharged}}} \quad (5.11)$$

where RA is % reduction in area, A_0 is initial area, A_f final area. The HEI was calculated by using RA of tensile specimens of with (-ch) and without charging. Table 5.16 shows the estimated HEI values for the base and weld metal. The hydrogen embrittlement susceptibility was found to be lower for the weld AF_W and SF_W.

Table 5.16: Area reduction of the tensile specimen with and without hydrogen charging

Specimens	Initial Area(avg)	Final area (avg)	%red. in area	HEI
X70	32.50	6.97	78.57	4.90
X70-ch	32.34	8.18	74.72	
AF_W	29.92	6.23	79.18	0.37
AF_W-ch	32.18	6.80	78.88	
SF_W	28.72	5.25	81.73	3.75
SF_W-ch	28.83	6.15	78.66	
CE_W	28.35	6.90	75.61	7.04
CE_W-ch	30.30	9.01	70.28	

Figure 5.30 illustrates the fractography appearance of ruptured tensile specimen with and without hydrogen charging. The visual appearance of the macrograph of shows more plastic deformation on the uncharged specimens as compared to the charged specimens. Also the fractography at higher magnification shows dimples resulting from micro-plastic deformation, along with the presence of micro-pores that serve as stress concentrators. These regions are the common initiation points for crack formation. Numerous micro-pores contribute to crack propagation in steel through the mechanism of void coalescence (Contreras et al., 2017). Mixed mode fracture (ductile + brittle) can be observed for the charged specimens. The fractography exhibits relatively flat surface features, suggesting a transition in the fracture mode from purely ductile to a mix of ductile and quasi-cleavage modes due to hydrogen charging. It is observed that the dimples become smaller and shallower, indicating a reduction in the extent of the ductile failure mode after hydrogen charging. This decrease in dimple size in ex-situ charged specimens can be attributed to the Hydrogen-Enhanced Localized Plasticity mechanism, where hydrogen reduces the maximum stress and strain required for void nucleation. Consequently, the lower formation energy accelerates void nucleation, leading to the formation of smaller dimples on the fracture surface (Yadav et al., 2023).

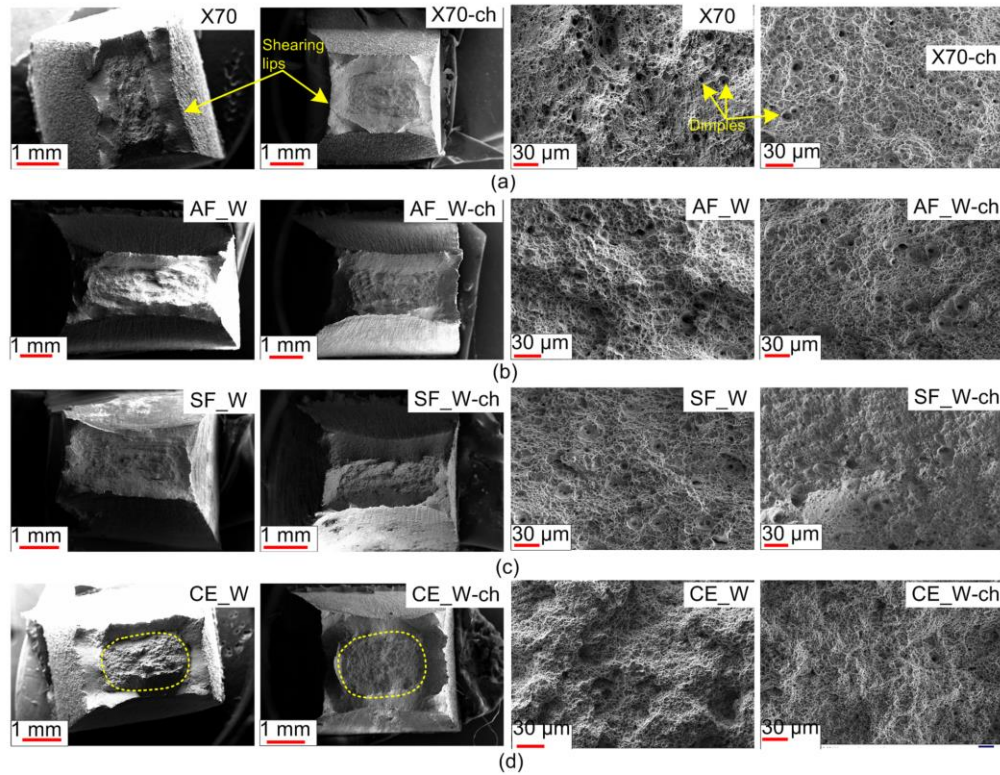


Figure 5.30 Fractography appearance of ruptured tensile specimen with (-ch) and without hydrogen charging
(a) X70 (b) AF_W (c) SF_W (d) CE_W

5.3.6 Metallurgical test

(a) Microstructural study

The microstructure of X70 base metal is shown in Figure 5.31 (a, b). The microstructure of X70 steel is composed of a dominant ferrite matrix, small pearlite-ferrite colonies, and a small amount of bainite. The X70 steel is microalloyed and produced using a thermomechanically controlled process. The process consists of controlled rolling followed by rapid cooling. The Mn-Mo-Nb microalloying along with controlled rolling results in the microstructure consisting of a combination of granular bainite or bainitic ferrite within the matrix (Singh et al., 2021). The microstructure of the SMAW weld is shown in Figure 5.31 (c-h). The weld C% is between 0.03 and 0.043 and the P_{cm} values are within the API limit. Mundra et al., discussed the phase transformation sequence for the low alloy steel welds. The weld solidification initially results in δ -ferrite (BCC) then it transforms to γ -(FCC) (Ghomashchi et al., 2015; Mundra et al., 1997). Figure 5.32 shows the generally accepted mechanism for microstructural evolution below 800°C. The FCC to BCC (α) transformation takes place cooling below 800°C. Cooling results in the coverage of prior austenite boundaries with allotriomorphic- α , further cooling promotes sideplates of Widmanstätten- α_w it occurs at the boundary of $\alpha - \gamma$. The acicular ferrite- α_a nucleates around the favorable non metallic inclusion sites. Absence of inclusions can also promote bainite- α_b instead of α_a . Finally, some martensite transformation occurs, resulting in a mixture of martensite-austenite (M-A phase). The above discussed mechanism remains the same for low alloy steel welds, and variations in the microstructure is governed by the nucleation and growth kinetics. The present work investigates the role of fluoro-alumino-silicate based laboratory developed flux. All welds have shown no signs of cracking, which can be attributed to the low P_{cm} value. The chemical composition of weld AF_W has Ni 1.26%, Mn 1.50%, Mo 0.215%, and Nb 0.365%. Figure 5.31 (c, d) shows thin grain boundary ferrites and fine acicular ferrite morphology, negligible Widmanstätten ferrite and polygonal ferrite (PF) have occurred. The weld SF_W has Ni 1.38%, Mn 1.32%, Mo 0.144% and Nb 0.246%. From Figure 5.31 (e, f), different orientations of fine ferrite morphology can be observed. The weld CE_W has low Ni, Mo and Nb content as compared to the

previous two welds. Figure 5.31 (g, h) shows comparatively thicker GBF and some polygonal ferrite morphology due to low Ni content. Fakheri et al. studied the role of Ni content and concluded that the AF increases and grain boundary ferrite reduces with the increase in Ni. Nickel has long been regarded to toughen weld metals, whereas its benefits are conditional (Fakheri et al., 2020). Adding nickel to C-Mn weld metal steadily increased the volume proportion of acicular ferrite at low manganese content (usually less than 1.0 wt-%). When manganese level was high, martensite and ferrite reduced acicular ferrite, resulting in second-phase aligned ferrite. While the manganese percentage was 1.4 wt-%, which is ideal for a C-Mn steel weld metal, toughness deteriorated as nickel amount approached 2.25 wt-% (Wang et al., 2002). The benefits of Ni content on the weld was studied, centreline crack with Ni 3.75% and Mn 1.55% observed, which shows benefit of Ni is conditional (Bhole et al., 2006).

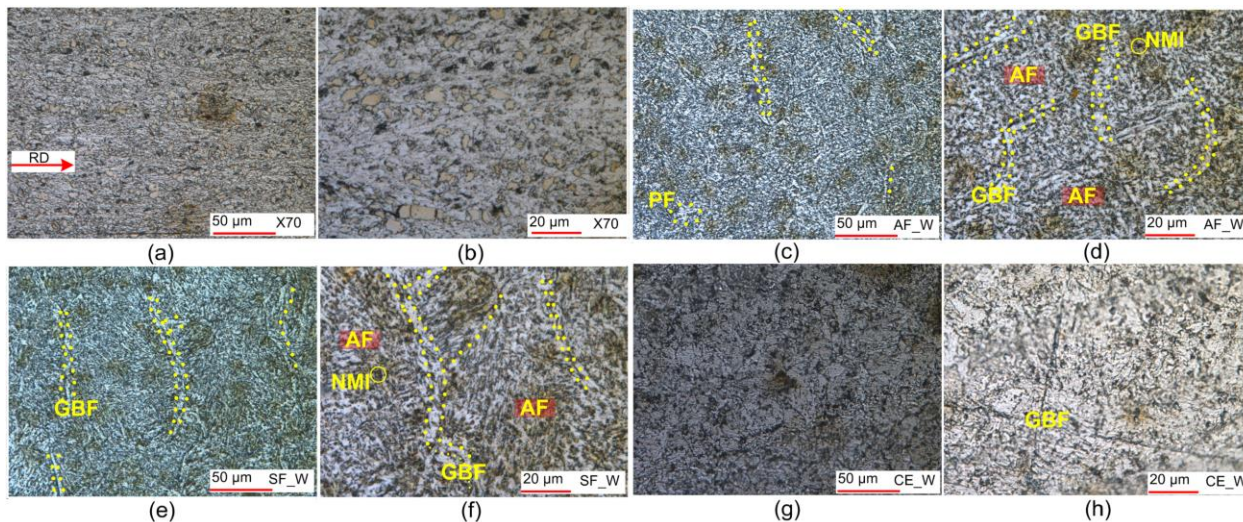


Figure 5.31: Optical micrograph of (a, b) X70 base metal, (c, d) weld AF_W, (e, f) weld SF_W, (g, h) CE_W

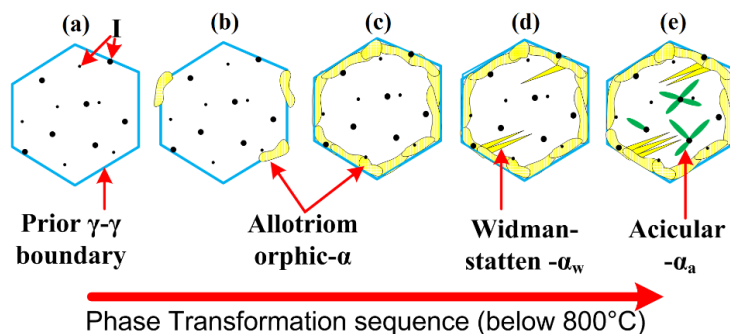


Figure 5.32: Phase transformation sequence for low alloy steel welds (Mundra et al., 1997).

The multi-pass SMAW process results in the weld structure, which majorly consists of reheated weld zone (fill pass). The cap pass is an as-welded zone and has undergone no thermal treatment, hence the columnar structure. The fill pass is reheated due to the next pass weld, near the reheated zone, coarse grain (CG) and fine grain (FG) are formed. Figure 5.33 (a) shows a schematic of the different zones in weldment, and Figure 5.33 (b) shows an optical micrograph of HAZ. The heat affected zone can be broadly categorized as coarse grain HAZ (CGHAZ) and fine grain HAZ (FGHAZ). The base metal microstructure near the fusion line is coarse due to high heat. The heat input effect on the naval high strength steel was investigated, it was concluded that increasing heat inputs resulted in coarsening of the grain and bainite lath, lowering impact toughness and mechanical characteristics. Whereas, at low heat inputs HAZ microstructure was fairly martensitic (Kumar et al., 2021) Figure 5.33 (c) shows image analysis of a micrograph. Using

the threshold function in ImageJ software, the variation of the white zone can be seen as whiter for the coarse zone and less white for the fine grain zone.

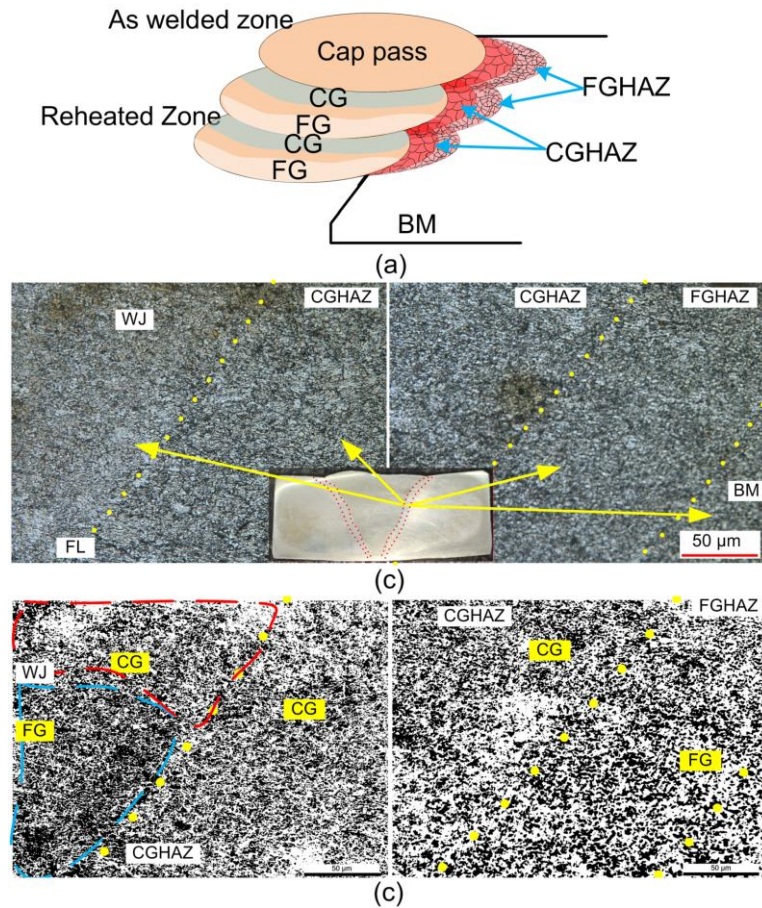


Figure 5.33: (a) Schematic of different weld zones in multi-pass weld, (b) optical micrograph showing weld and HAZ, (c) image analysis showing different zones in weldment.

Previous investigations have reported that the Ni content is correlated with M-A islands. The investigation by Mosallae et al. also reported that the increase in Ni content increases the M-A islands. Ni content reduces the decomposition temperature of $\gamma - \alpha$ hence delaying the diffusional transformation. The remaining austenite increases with higher Ni content (Mosallae et al., 2021). In Figure 5.34, M-A islands colonies can be observed in the weld micrograph.

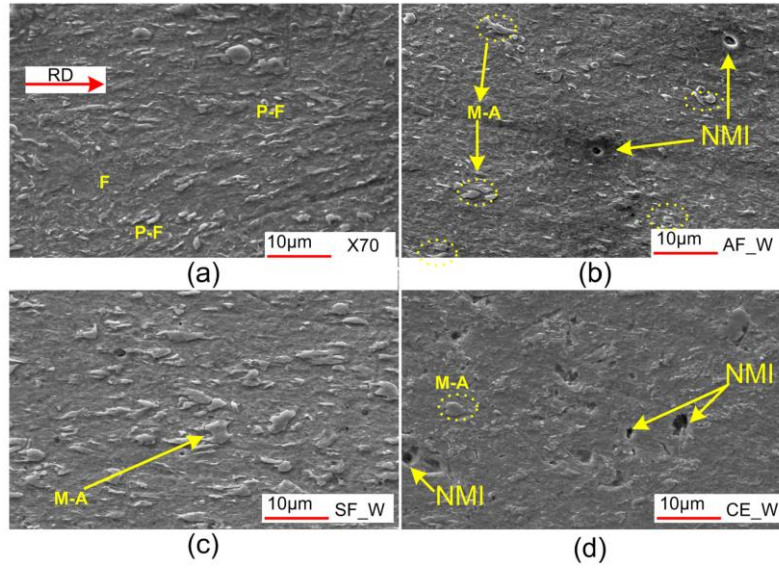


Figure 5.34: SEM images of (a) X70, (b) AF_W, (c) SF_W, (d) CE_W

Figure 5.35 presents the EBSD analysis of the weldment, providing critical insights into the grain morphology, boundary characteristics, and crystallographic texture across the base metal, HAZ, and weld metal. The analysis highlights the evolution of microstructural features induced by welding thermal cycles. The BM exhibits equiaxed grains with a relatively random orientation, characteristic of a solution-annealed microstructure (Figure 5.35(a)). The AF_W region displays a finer, more homogeneous grain structure with predominantly equiaxed morphology, suggesting rapid solidification under non-equilibrium thermal conditions. In contrast, the HAZ exhibits grain coarsening and heterogeneous orientation, reflecting partial recrystallization and grain growth phenomena induced by localized thermal exposure during welding. Figure 5.35(b) shows the detailed grain orientation maps for the respective regions. The distribution of crystallographic orientations reveals that the weld region (AF_W) has a more randomized texture compared to the base metal, attributed to the melting and resolidification process during welding. The HAZ retains partially the initial texture but with noticeable grain coarsening.

Figure 5.35(c) shows the grain size distribution, where BM exhibits finer grains, predominantly centered around 4–6 μm . In contrast, HAZ grains are significantly coarser, with diameters extending up to 25 μm , indicating grain coarsening due to thermal exposure during welding. The AF_W region shows a finer and narrower distribution, mostly between 5–10 μm , attributed to rapid solidification during welding that restricts grain growth. Thus, while BM retains its as-received fine grain structure, HAZ undergoes grain growth due to localized heating above recrystallization temperature without complete phase transformation. AF_W, experiencing rapid solidification, exhibits refined equiaxed grains improving strength through grain boundary strengthening. Grain boundary characteristics and misorientation distribution are presented in Figure 5.35(d). The misorientation profiles indicate that BM, HAZ, and AF_W are dominated by low-angle grain boundaries (LAGBs) ($<15^\circ$) with fractions of 72.31%, 73.30%, and 72.40% respectively, suggesting the presence of significant substructures and strain accumulation. The slight increase in LAGBs in the HAZ reflects recovery processes initiated by the welding thermal cycle, while the AF_W retains a similar LAGB fraction to BM due to rapid cooling preventing grain boundary migration and transformation to high-angle grain boundaries (HAGBs) (Alipooramirabad et al., 2020; Wang et al., 2018).

Figures 5.35(e) and 5.35(f) depict the detailed grain boundary maps for BM and AF_W, respectively, where boundaries are color-coded based on misorientation angles. The grain boundaries are color-coded: red lines represent low-angle grain boundaries (LAGBs, 1° – 5°), green lines represent medium-angle boundaries (5° – 15°), and blue lines denote high-angle grain boundaries (HAGBs, $>15^\circ$). In the BM region (Figure 5.35(e)), the boundary analysis reveals that

approximately 62.3% of the boundaries fall within the 1°–5° range, 9.1% within 5°–15°, and 28.5% correspond to HAGBs (>15°). This high proportion of LAGBs in the BM is indicative of a heavily worked microstructure that has undergone partial recovery during solution treatment, leading to well-developed subgrain structures. In contrast, the weld metal (AF_W) (Figure 5.35(f)) shows 61.0% of boundaries in the 1°–5° range, 10.7% between 5°–15°, and 28.4% above 15°. Although the total fraction of LAGBs and HAGBs remains comparable to the BM, a slight increase in medium-angle boundaries (5°–15°) is observed in AF_W. This increase suggests that during the solidification of the weld metal, subgrains formed with slight misorientations, but rapid cooling prevented further growth into fully recrystallized grains with high-angle boundaries. The dense network of fine subgrains observed in AF_W reflects the influence of non-equilibrium solidification processes typical of fusion welding.

Pole figure (PF) and inverse pole figure (IPF) texture analyses are shown in Figures 5.35 (g-i). In the BM, the PFs reveal a weak but distinguishable rolling texture with mild fiber orientations along <001> and <111> directions. The maximum multiple of uniform density (MUD) reaches approximately 6.4, indicating moderate texture intensity due to prior thermomechanical processing (Figure 5.35(g)). In contrast, the AF_W shows relatively random texture with scattered orientations, and a slightly higher MUD value (~9.0), reflecting solidification-induced texture under non-equilibrium conditions (Figure 5.35(h)). The HAZ exhibits the texture with MUD values as ~8.3, indicative of texture due to recrystallization and grain growth driven by thermal cycles during welding (Figure 5.35(i)). Such texture evolution affects anisotropy in mechanical and corrosion properties, which is critical for service performance. Significant grain refinement in the weld zone, grain growth in the HAZ, dominant subgrain formation (LAGBs), and weakening of texture intensity collectively highlight the complex interplay between welding thermal cycles and microstructural evolution.

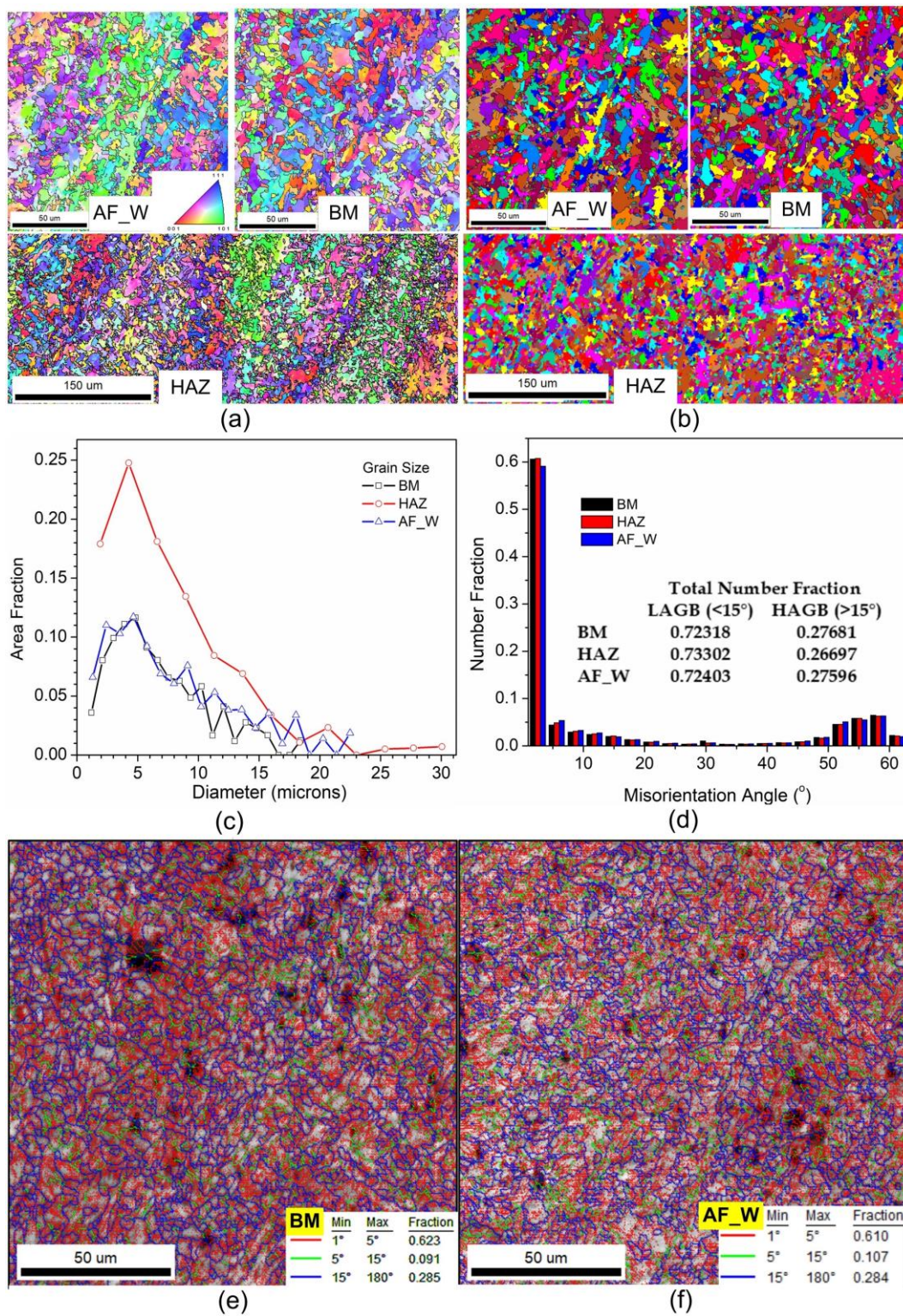


Figure 5.35: EBSD analysis of weldment (a) IPF maps, (b) grain orientation maps, (c) grain size measurement, (d) Total number fraction of HAGB and LAGB, (e) grain boundary map base metal, (f) grain boundary map weld

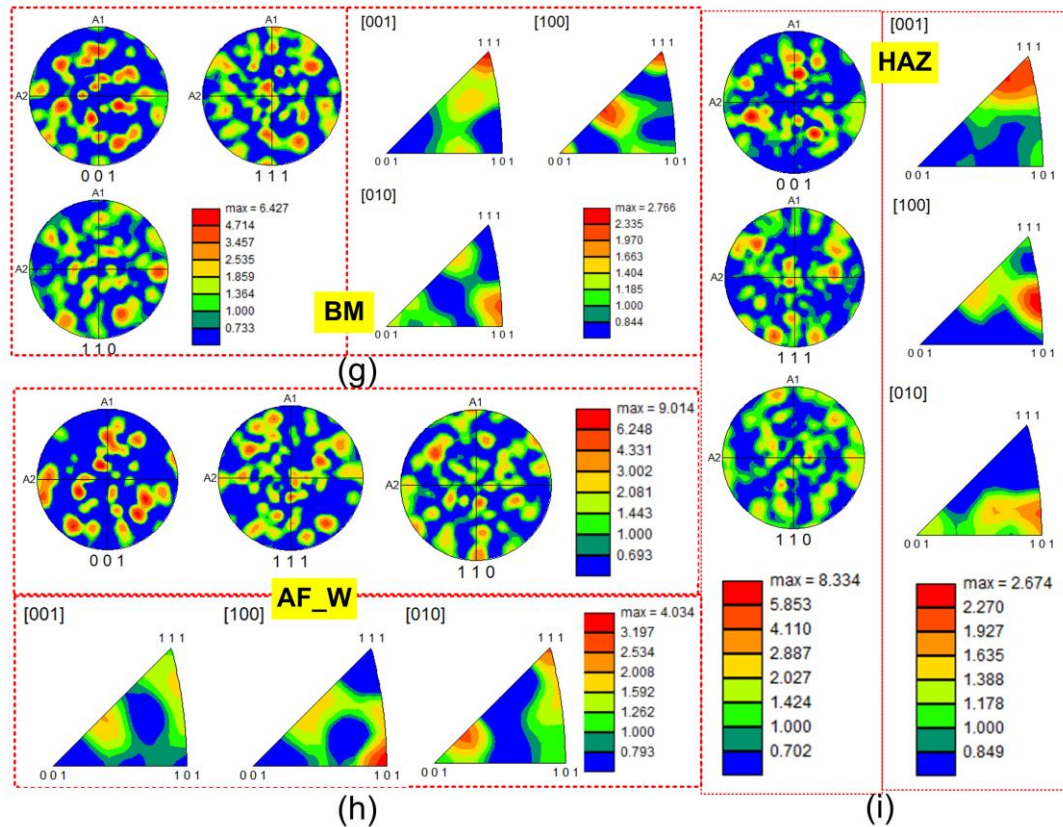


Figure 5.35: Pole figures and IPF texture (g) base metal, (h) weld metal, (i) HAZ

(b) Thermodynamic assessments

The MUCG83 thermodynamic model was developed by Peet M. and Bhadeshia, H.K.D.H. The Python code of the MUCG83 thermodynamic model available on GitHub by Nishikawa A. was used to calculate the TTT and CCT diagrams (Nishikawa; Peet). Figure 5.36 (a) shows the comparison of the CCT curve predicted for weld and base metal composition. It can be seen in the CCT curve, for weld AF_W and SF_W, ferrite-pearlite (F+P) nose is shifted towards the slow cooling rate, as compared to weld CE_W. For same cooling curve, the transformation time for austenite to ferrite + pearlite decreases for the AF_W and SF_W as compared to CE_W. This happens due to the shift in F+P nose, which reduces the F+P content in weld. The selected cooling curve is at the same location for all curves and is shown only for the comparison, it does not represent the actual cooling rate. Figure 5.36 (b) shows the TTT diagram generated for the weld and X70 base metal. The martensitic start temperature (M_s) was 454°C and the bainitic start temperature (B_s) was 575°C for the weld AF_W. The M_s and B_s for SF_W is 458°C, 579°C, and for CE_W it is 473°C, 612°C respectively. Due to the presence of the alloying element, the M_s is reduced to $17 \pm 2^\circ\text{C}$ as compared to M_s of CE_W. The martensitic start temperature (M_s) indicates when austenite begins to change into martensite, during cooling. This low M_s delays the formation of martensite which is considered a brittle phase, the presence of Ni content results in the retained austenite with lower transformed martensite. The upper limit of the bainite (TTT) curve is Widmanstätten start (W_s) temperature, the W_s for AF_W and SF_W is 695°C and 700°C whereas for CE_W it is 725°C. The equilibrium phase diagram (Figure 5.36 (c)) for the weld was generated using the OpenCalphad technique (Sundman et al., 2015), which was implemented in Materials Square (Virtual Lab. Inc., n.d.).

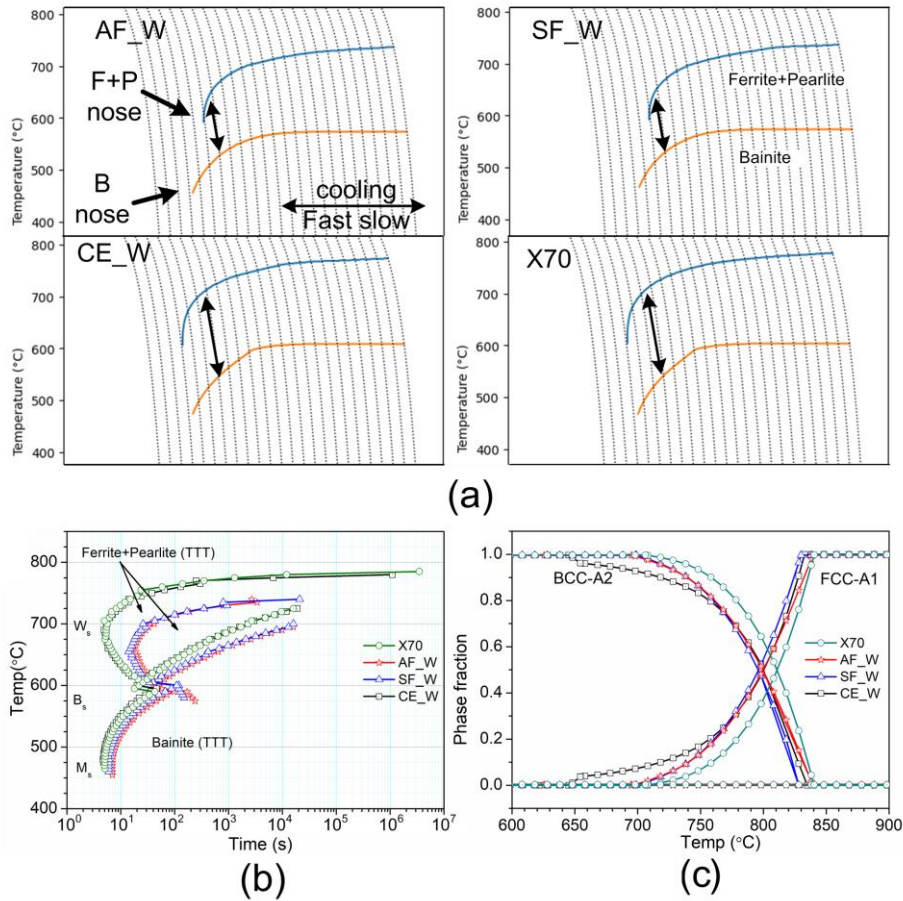


Figure 5.36: (a) Comparison of CCT curve, (b) TTT curves using MUCG83 model, (c) equilibrium phase diagram of X70 and weld (MatSQ FE 2.0)

(c) Weld inclusions

SEM-EDS investigation of the specimens was done to investigate the chemistry and size of the inclusions present in the weld. Welding procedures with fluxes, such as SMAW, frequently introduce inclusions into the steel matrix. These inclusions are unavoidable and can affect the weld positively or negatively depending on their type, size, and composition. The inclusions can consist of simple oxides, sulfides, nitrides, and complex multiphase inclusions. The type of these inclusions and the grain boundary size influence the production of the desired intragranularly nucleated acicular ferrite phase.

Figure 5.37 shows EDS and area mapping of specimens. EDS demonstrates that the inclusion is rich in aluminum, silicon, and oxygen. Trace quantities of Mn, and Ni were also detected. The flux coating comprises Al_2O_3 , which is the primary source of these inclusions. Although Al_2O_3 is not regarded as an active nucleation site, its interaction with other elements makes it an ideal nucleation site. Galaxite inclusions, can occur in Al-deoxidized Mn-containing steels, are far more effective at acicular ferrite nucleation than alumina. As a result, inclusions rich in Al and O, as well as manganese-rich weld pools, increase the likelihood of suitable nucleation sites for acicular ferrite. Several theories have been proposed in the literature to explain the formation of acicular ferrite at inclusions. These processes include decreased interfacial energy, which facilitates heterogeneous nucleation on inclusion surfaces, as well as epitaxial nucleation on inclusions with high ferrite coherency. In this context, there are two types of nucleation. The first type is nucleation generated by thermal stresses at the inclusions, which are caused by the differences in thermal expansion coefficients between the inclusions and the steel matrix. The second type is nucleation, which happens when solutes are depleted in the matrix at inclusions (Loder et al., 2017).

During SMAW, the interaction of slag and the metal help transmit the nonmetallic inclusions (NMIs) to the weld. Achieving a suitable acicular ferrite shape requires an ideal number of NMIs. Loder et al. analyzed past studies and discovered that NMIs of 0.5-5 μm in size have a high possibility of nucleation, but NMIs that are too large or too small are less effective (Loder et al., 2017). Figure 5.38 shows the inclusion size estimation of weld and X70, it can be observed that the inclusion size is below $<5 \mu\text{m}$ for all welds. So, the flux chemistry is deciding factor to promote active NMIs in the weld.

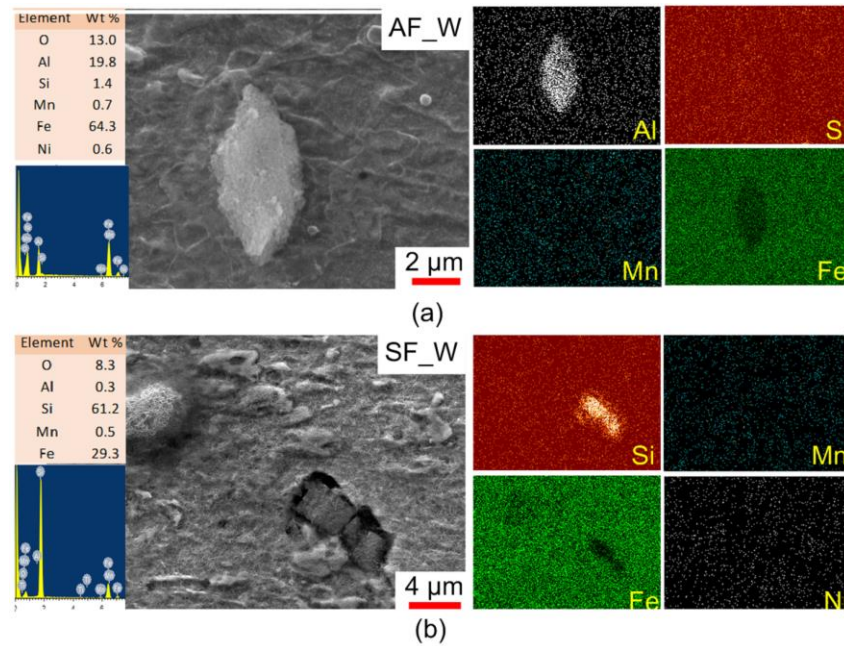


Figure 5.37: EDS investigation of the inclusions present in weld (a) AF_W, (b) SF_W

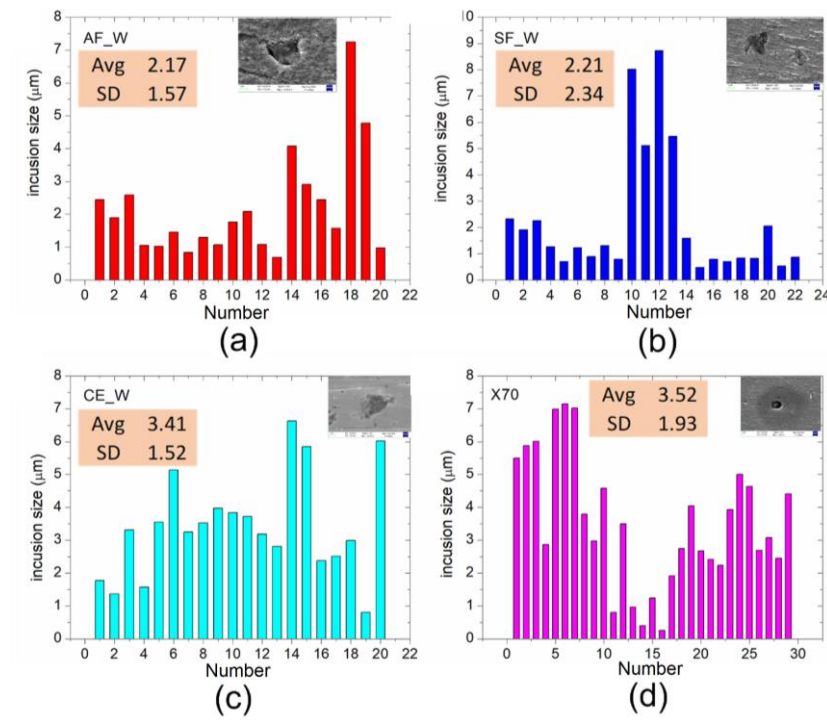


Figure 5.38: Comparison of non-metallic inclusion sizes present in weld and base (a) AF_W, (b) SF_W, (c) CE_W, (d) X70

5.4 ANALYSIS OF DUCTILE FRACTURE

As per the results and discussion on the weld characterization, AF_W was selected. This section has discussed the single edge notch bend experiments and its modeling using finite element analysis of base metal (BM) X70 and weld metal (WM) AF_W.

5.4.1 Material property

The uniaxial tensile test was performed for the BM and WM. The extracted true stress vs. true plastic strain data is shown in Figure 5.39. The BM X70 has σ_{YS} and σ_{UTS} of 504.87 MPa and 625.38 MPa respectively, with strain hardening coefficient $n = 0.13$, and strength coefficient $K = 928.7$ ($\sigma = K\epsilon_t^n$). For the weld, $\sigma_{YS} = 494.49$ MPa, $\sigma_{UTS} = 609$ MPa, $n = 0.11$, and strength coefficient $K = 870$. For both BM and WM, the Youngs modulus was 210 GPa and the poisons ratio was 0.3. For the Abaqus/Explicit analysis, the density of the steel was considered to be 7.8×10^3 kg/m³. The FEM simulation using the GTN damage model requires elastic-plastic data and nine GTN parameters which are discussed further.

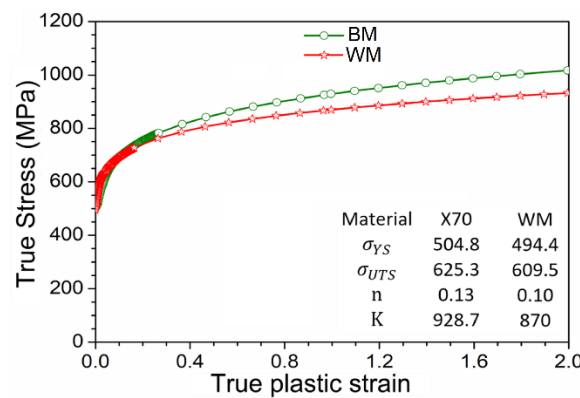


Figure 5.39: True stress vs. true plastic strain curve for BM and WM

5.4.2 Regression analysis and parametric study

Abbasi et al. utilized the response surface method (central composite design) to fit the six GTN parameters, i.e., ϵ_N , S_N , f_N , f_o , f_c and f_f . Their objective was to simulate the forming limit diagram (Abbasi et al., 2012). The ductile fracture of the tensile test of SAE1010 plain carbon steel under different stress states was investigated, the study calibrated f_N , f_o , f_c and f_f parameters while keeping the remaining parameters constant (Gholipour et al., 2019). It can be concluded that the GTN parameter identification using statistical methods is an effective tool. Present work has tried to reduce the unknown parameter to f_o , f_c and f_f . Dutta et al. concluded that the f_o should not be calculated from the Franklin formula (Dutta et al., 2008). The VVF nucleation f_N can be calculated using Franklin formula (Franklin, 1969; Qiang et al., 2019; Zhang et al., 2000). Although researchers have tried to obtain relationships between f_o , f_c and f_f , they cannot be used for every material due to the variation in damage behavior. A quadratic relation between the input parameter with the materials response can be developed. The parameters f_o , f_c and f_f have shown significant influence on crack growth and load-CMOD curve. Table 5.17 shows the coefficients of the developed quadratic regression equation. The analysis of variance (ANOVA) table is provided in the appendix (Table A13). Figure 5.40 shows a 2-dimensional plane strain analysis with CPE4R element and failure criteria for crack growth when the void volume fraction reaches final void volume fraction.

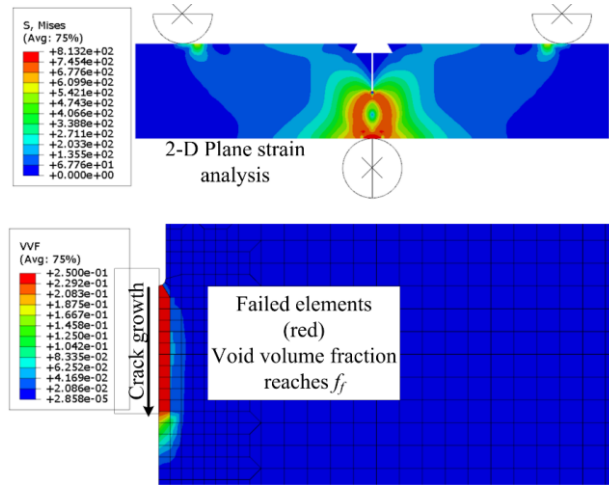


Figure 5.40: A 2-dimensional plane strain analysis with CPE4R element and failed element with void volume fraction reaches final void volume fraction.

Table 5.17: Coefficients of regression equation

Obj_1		$(1 - f_o)$	f_c	f_f	$(1 - f_o) \times f_c$
	-1.49E+06	2.99E+06	5.11E+03	1.52E+03	-5.17E+03
	$(1 - f_o) \times f_f$	$f_c \times f_f$	$(1 - f_o)^2$	f_c^2	f_f^2
	-1.51E+03	4.15E+01	-1.50E+06	1.06E+02	-2.20E+01
Obj_2		$(1 - f_o)$	f_c	f_f	$(1 - f_o) \times f_c$
	-2.31E+06	4.65E+06	-1.62E+04	-2.02E+04	1.58E+04
	$(1 - f_o) \times f_f$	$f_c \times f_f$	$(1 - f_o)^2$	f_c^2	f_f^2
	2.01E+04	2.22E+02	-2.34E+06	9.38E+02	1.08E+02
Obj_3		$(1 - f_o)$	f_c	f_f	$(1 - f_o) \times f_c$
	-2.15E+06	4.30E+06	2.69E+03	8.59E+03	-2.83E+03
	$(1 - f_o) \times f_f$	$f_c \times f_f$	$(1 - f_o)^2$	f_c^2	f_f^2
	-8.61E+03	1.19E+02	-2.15E+06	2.91E+02	-2.58E+01

The desirability function approach (Del Castillo et al., 1996; Derringer et al., 1980) was used to optimize the Obj_1, Obj_2 and Obj_3. The aim was to achieve Obj_1 = 0, Obj_2 = 0 and Obj_3 = 0 simultaneously.

Figure 5.41 shows the contour plots and perturbation plots. According to the perturbation plot, the increase in $(1 - f_o)$ and f_c has a relatively greater effect than the increase in f_f . The starting of the load-CMOD curve up to the maximum load is governed by the J2 plastic theory; therefore, no effects are observed with VVF variation. After the maximum load, metal matrix experiences stress around the inclusion particles, which acts as nuclei. The mechanism of nucleation, growth, and coalescence of void is captured by the VVF parameters. The increase in relative density $(1 - f_o)$ or decrease in initial VVF f_o leads to improvement of load-carrying capacity after maximum load. Similar effects on crack growth can be expected; increases in $(1 - f_o)$ lead to improved crack growth resistance. The relative density equal to 1 refers to a metal with zero inclusions; hence, no void nucleation sites. The critical VVF f_c is a material response during void coalescence. Unlike f_o , the f_c is not a material property. The high f_c value results in increased the load carrying capacity, i.e., delayed start of void coalescence. The increase in f_c increases the crack growth resistance. The final VVF f_f is a limiting value; the fracture is completed when $f = f_f$. The effect of f_f on load-carrying capacity and crack growth is low but noticeable.

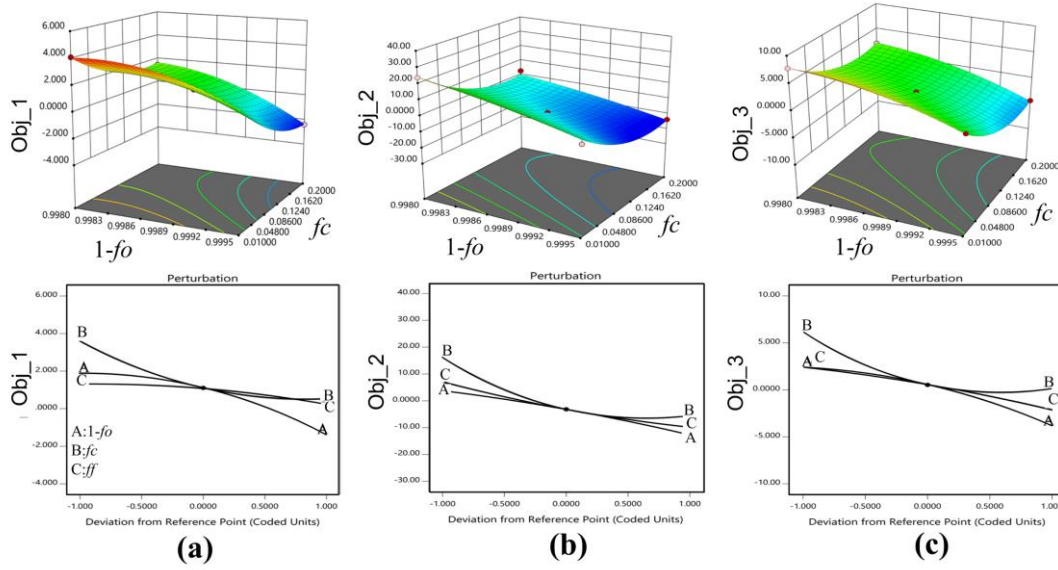


Figure 5.41: Contour plots and perturbation plots of (a)Obj_1 (b) Obj_2, (c) Obj_3

The SENB simulations with GTN damage models are highly sensitive to mesh size. Mesh size effect was studied, in the fracture process zone mesh size of 0.05, 0.1, 0.15, 0.20, and 0.25 mm were tested. Figure 5.42 shows the material response through load vs CMOD and CMOD vs. crack growth (Δa_{un}) curves for different element sizes. Use of smaller element reduces the load carrying capacity of the material. Here, the mesh size resembles the mean spacing between the second-phase particles in the metal matrix. The experimental results were in good agreement with the 0.2 mm mesh. With same GTN parameters, large mesh size offers higher crack growth resistance as compared smaller mesh size.

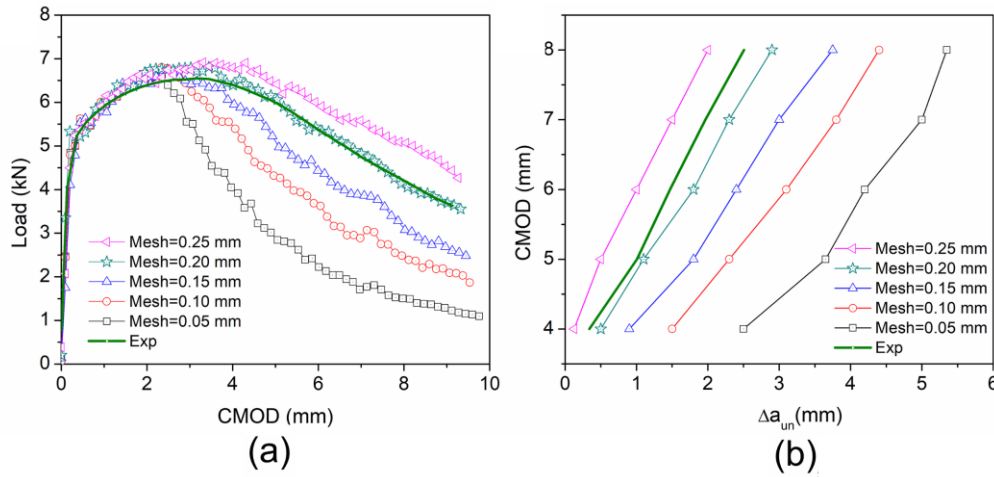


Figure 5.42: Effect of mesh size on BM SENB $a_0/W=0.50$ (a) Load vs. CMOD curves (b) CMOD vs. Δa_{un}

The calibrated GTN parameters for the BM and WM are shown in Table 5.18. The weld SENB has shown fracture instability before tearing, so crack growth objective was not matched with simulated crack growth. The weld SENB simulation was targeted to match the experimental load-CMOD results. The parameters f_0 and f_N are found to be higher in weld than X70, which can be attributed to increase in the inclusions due to shielded metal arc welding. Shielded metal arc welding utilizes flux for shielding. During welding, the flux is melted, known as slag. This slag interacts with the molten metal. Slag particles that were unable to escape the weld pool due to insufficient floatation are entrapped in the solidified weld pool resulting in the rise in the inclusion amount.

Table 5. 18: Calibrated GTN model parameter for X70 and weld

	q_1	q_2	q_3	f_o	f_N	f_c	f_f	ε_N	S_N	l_c
BM	1.5	1	2.25	0.00114	0.0010	0.178	0.25	0.3	0.1	0.2 mm
WM	1.5	1	2.25	0.00700	0.0018	0.030	0.40	0.3	0.1	0.1 mm

5.4.3 Validation of GTN parameters with experiments

(a) Tensile test

The GTN model parameters (Table 5.18) were used to predict the flat notch tensile test of BM and WM. Figure 5.43 (a, b) shows the triaxiality state of flat tensile and flat notch tensile tests and fractography. The plot between PEEQ vs. triaxiality shows that the flat notch tensile test has comparatively high triaxiality due to the notch geometry. Fractography comparison shows small dimples for flat notch tensile and comparatively larger dimples for flat notch tensile test. The steel generally contains large second-phase particles (sulfides, oxides) responsible for primary voids and small carbides as secondary voids. Low stress triaxiality results in void sheeting mechanisms with smaller primary voids linked with nucleated secondary voids. High stress triaxiality promotes internal necking mechanisms causing large primary voids where inter-void ligaments neck and fail, with little or no nucleation of secondary voids (Besson, 2010).

Figure 5.43 (c, d) shows the comparison of GTN results with experimental results on load displacement curve of BM and WM. Here it is noteworthy that the GTN parameters calibrated using only SENB $a_0/W = 0.50$ results, however, the model has predicted damage initiation point in flat notch tensile test fairly accurately.

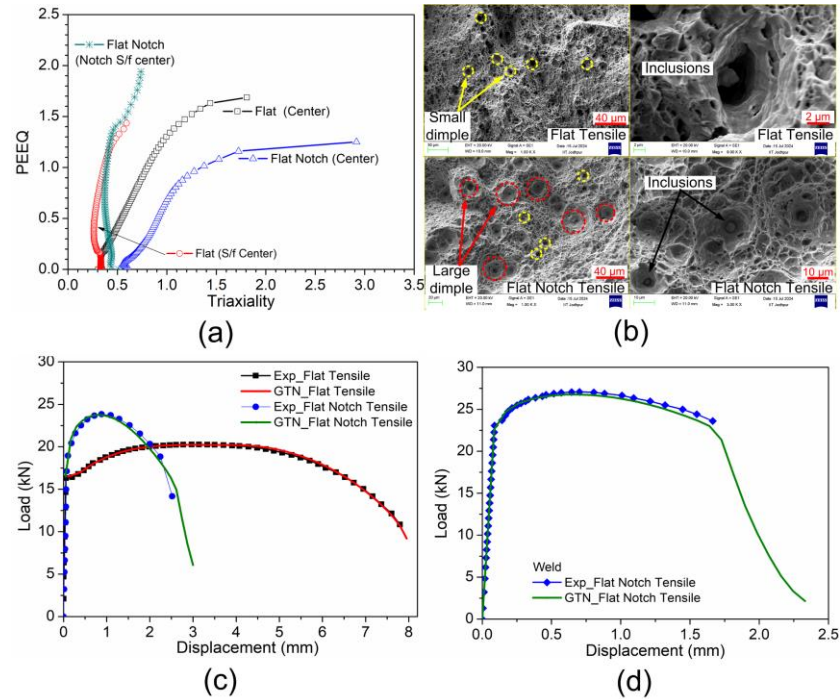


Figure 5.43: (a) Triaxiality of flat tensile and flat notch tensile specimen (b) Fractography showing the effect of triaxiality. Comparison of experimental and simulated tensile load-displacement (c, d) BM and WM

(b) SENB test

The DIC analysis was performed to obtain the CMOD data from the SENB tests. The crack growth obtained using image analysis does not consider blunting, so initially the crack growth was termed as uncorrected crack growth (Δa_{un}). The incremental load-CMOD data was used to calculate the J – integral value. The formulas used for J integral and CTOD calculation have been

provided in the earlier section and appendix. Crack tip opening displacement (CTOD) values till the initial crack length a_0 was calculated, the corrected crack growth was calculated using $\Delta a = \Delta a_{un} + CTOD/2$. The corrected crack growth includes the initial blunting effect when the crack growth is yet to begin. Load-CMOD, load- Δa_{un} , CMOD- Δa_{un} , and J- Δa curves were plotted for $a_0/W = 0.50$, and $a_0/W = 0.25$ (Figure 5.44). There are different methods proposed by the researchers to calibrate the GTN model parameter, which also includes round-notch tensile test. Present work utilizes high constraint SENB results only to calibrate the f_o , f_c and f_f , along with the f_N calculated using Franklin's formula. The details of the simulation and design matrix are already provided in the experimentation section. The calibrated GTN model parameter was used to simulate BM SENB $a_0/W = 0.50$, and $a_0/W = 0.25$. Similar to experimental tests, the J integral was calculated, and the load-CMOD, load- Δa_{un} , CMOD- Δa_{un} , and J- Δa curves were plotted. Figure 5.44 (a) shows experimental and GTN predicted load-CMOD results. EP, i.e., elastic-plastic results that are based on J2 plastic theory, were also included as a reference to show the effect of no damage consideration. Figure 5.44 (b-d) shows experimental and simulated load- Δa_{un} , CMOD- Δa_{un} , and J- Δa curves. It was observed that $a_0/W = 0.50$ simulation has a good fit, whereas $a_0/W = 0.25$ has slight variation in J- Δa . Overall, the GTN parameters have resulted in a good estimation of crack growth, CMOD, and J value.

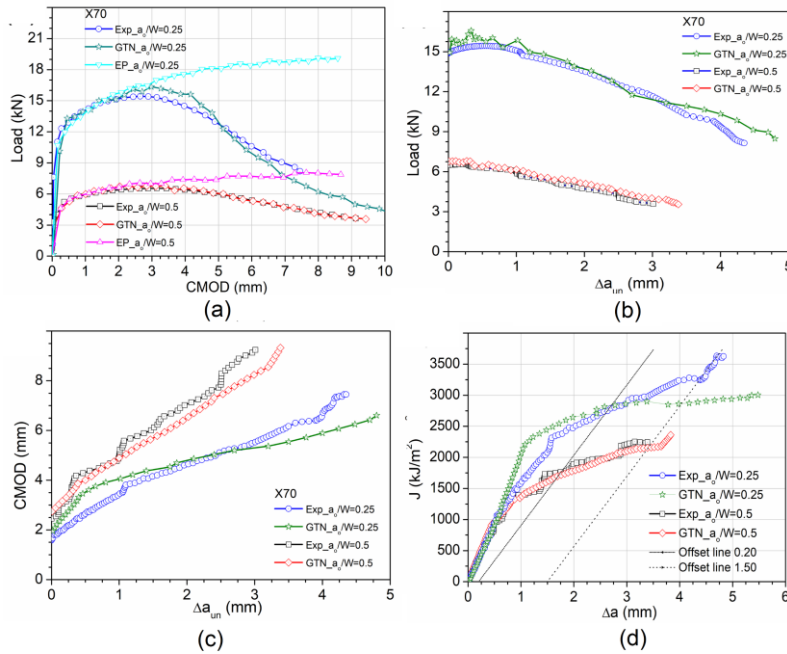


Figure 5.44: Comparison of experimental and simulated results of SENB, (a) Load-CMOD curve, (b) Load- Δa_{un} curve, (c) CMOD- Δa_{un} curve, (d) J- Δa curve of BM

Due to increased inclusions from the shielded metal arc welding, fracture instability was observed before tearing, also known as pop-in. Fracture toughness instability J_{Qc} was calculated. Figure 5.45 (a) shows the experimental load-CMOD curve, the sudden drop is known as pop-in, and Figure 5.45 (b) shows the calculated J_{Qc} value. It can be seen that pop-in is observed after the maximum load. The weld GTN parameters were used for WM SENB $a_0/W = 0.50$, and $a_0/W = 0.25$ simulation. The load-CMOD curve was generated for both constraints; Figure 5.45 (a) shows a poor fit of load-CMOD for low constraint SENB. This discrepancy occurs due to the homogenous material consideration in FPZ whereas weld material undergoes heat cycle resulting inhomogeneity in FPZ. A Mod_FPZ was developed that imitates the effect of multi-pass weld heat cycles. The details of Mod_FPZ are provided in previous section. In Mod_FPZ, zero hardening properties have been assigned at definite intervals. The same Mod_FPZ was used for both SENB constraints, and GTN model parameters were also kept the same. The J_{Qc} values for

the simulations were calculated at the pop-in. Results presented in Figure 5.45 (a, b) suggest that the Mod_FPZ is an effective approach for capturing pop-in behavior. The Mod_FPZ has more effect for low constraints ($a_o/W = 0.25$) as compared to high constraints ($a_o/W = 0.50$). Due to the fracture toughness instability, crack growth was not simulated properly.

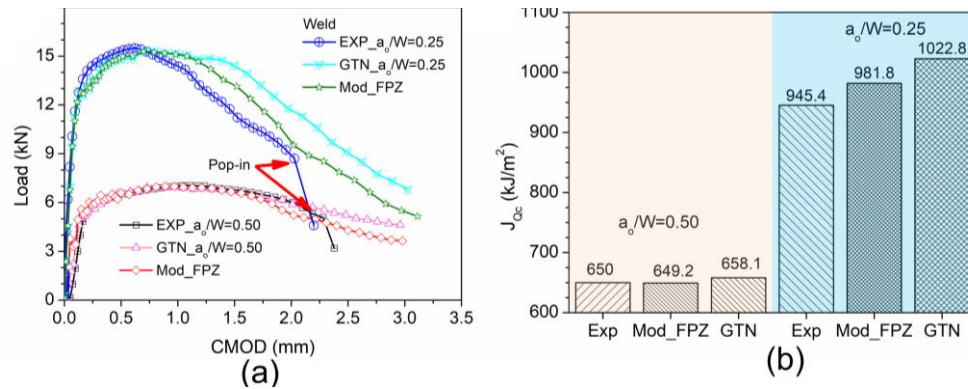


Figure 5.45: Comparison of experimental, GTN + Mod_FPZ, and GTN results of weld SENB, (a) Load-CMOD curve, (b) J_{Qc} values for WM SENB

5.4.4 Validation on different geometries from literature

It was observed that the calibrated GTN model parameters, with critical length parameter, can produce satisfactory results for the experimented flat notch tensile and SENB $a_o/W = 0.25$. For further validation of the parameters, the results obtained by (Paredes et al., 2016) were simulated. They studied the post-initiation softening application in the initiation and propagation of ductile cracks in thick sections. Their work has studied X70 pipelines steel using notch round tensile tests and SENT specimens. The elastic-plastic inputs were taken from their work, whereas GTN model parameters of the present work were used. Since the materials are the same plasticity and damage behavior can be expected to be similar, although some variations are always present with the same grade of steel having different manufacturers. Tensile tests of notch round bar (NRB) with 1 mm and 0.5 mm notches were simulated. An axisymmetric model with 4 noded axisymmetric elements (CAX4R) was developed. The element size was 0.2 mm. The gage length was 40 mm, so using half symmetry, 20 mm length was modeled. Figure 5.46 (a) shows the triaxiality state of NRB1 and NRB0.5 after 0.2 mm displacement in the boundary conditions. It can be seen that NRB0.5 has higher triaxiality as compared to NRB1. The NRB specimen on the monotonic uniaxial test shows a sharp damage initiation point. Therefore, high triaxiality of NRB has also often been employed by the various researchers to calibrate the GTN parameter. Figure 5.47 (a) shows the simulated load displacement curve. It can be seen that the damage initiation is accurately captured with calibrated BM GTN model parameters. The single edge notch tension (SENT) tests are low constraint tests as compared to the SENB test. The fracture toughness obtained using SENT tests is close to the full-scale tests. The width for SENT simulation was $W=20$ mm, ($a_o/W = 0.35$, $H=10W$, and $B_N = 17.94$). A 4 noded 2-dimensional plane strain reduced integration (CPE4R) model was developed (Figure 5.46 (b)). A small protrusion of 0.05 mm was given for smooth fracture initiation at the sharp crack tip. The CTOD was recorded from the one node above the crack tip in the symmetry plane (Paredes et al., 2016). The simulated data of CTOD- Δa between the 0.5 and 1.5 crack growth was used to calculate the power law constants. . Figure 5.47 (b) shows the load-CMOD and CTOD- Δa . The simulated CTOD- Δa results are in good agreement.

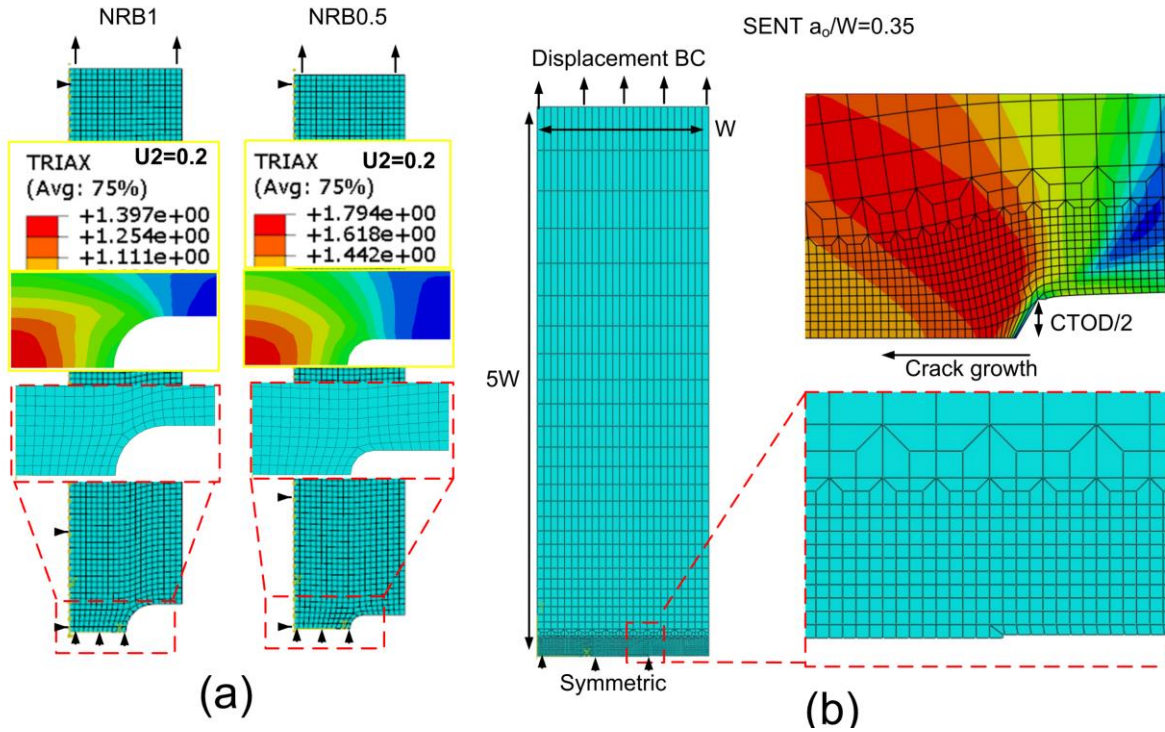


Figure 5.46: Simulation for the testing of X70 GTN model parameters (a) Axisymmetric model for NRB1 and NRB0.5 tensile test (b) SENT 2-D simulation model meshing and CTOD location.

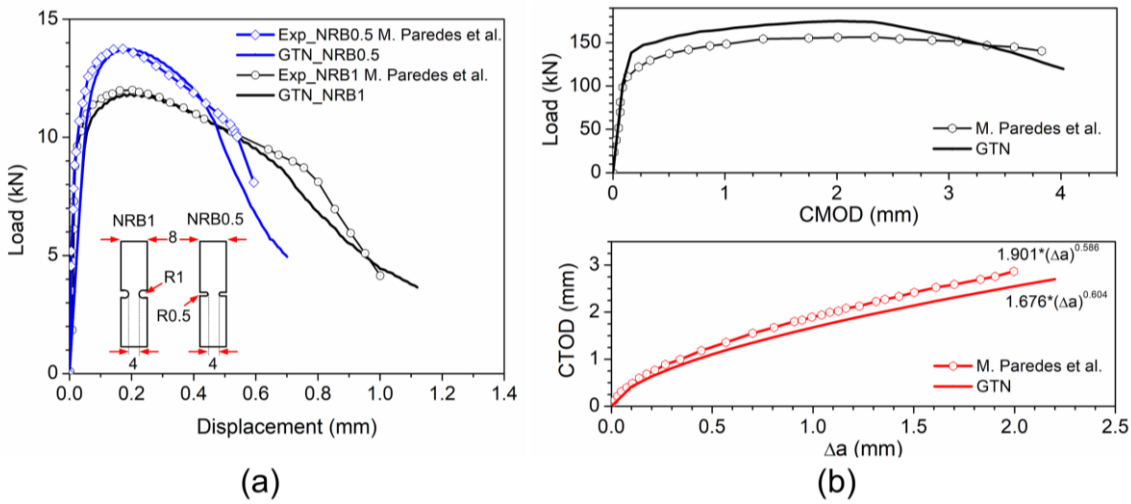


Figure 5.47: (a) Validation of GTN model parameters on round notch tensile load displacement results (b) Validation of GTN model parameters on SENT test, Load-CMOD curve, and CTOD- Δa curve (Paredes et al., 2016).

5.4.5 Effect of crack tip sharpness

The SENB specimens are generally fatigue-pre-cracked to induce the sharp crack tip. Targeting initial crack depth a_0 using fatigue pre-cracking is difficult, which can be obtained by using precise EDM cut. Preparation of precise sharp crack depth is a need for standardization and homogenization. Various researchers have investigated the role of crack sharpness on fracture toughness (Kim et al., 2018; Marines-Garcia et al., 2019; Schindler et al., 2014). Park et al. reported the fracture toughness with different crack tip acuity. The results indicate that crack tip sharpness has a considerable impact on toughness assessment; particularly during the blunting stage, toughness measures have been enhanced (Park et al., 2017). Figure 5.48 (a) shows the schematic

of crack tip blunting and initiation location in J- Δa curve. Sharp crack tip undergoes blunting followed by initiation and propagation. The EDM wire diameter created a slightly blunted crack tip; due to this, the initial blunt fracture toughness at initiation is increased.

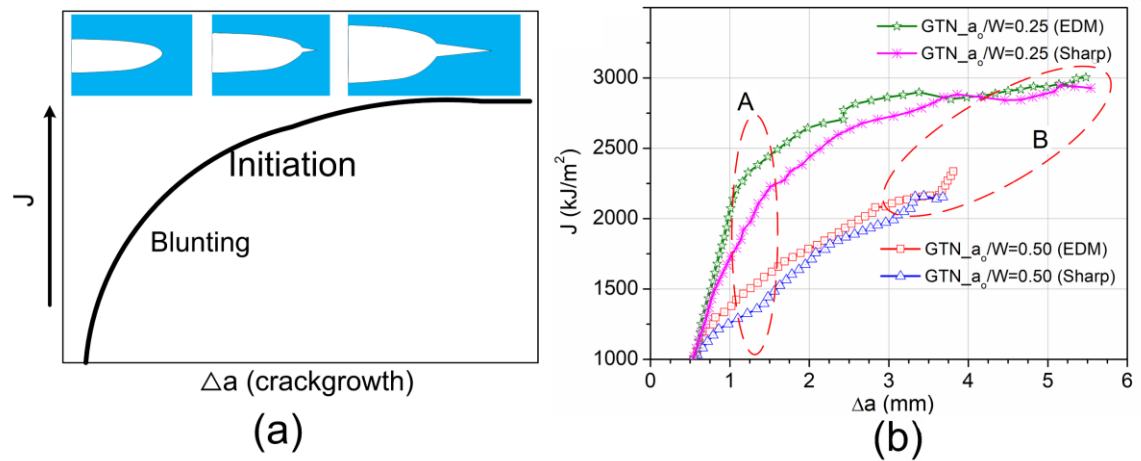


Figure 5.48: (a) Schematic of J- Δa curve showing blunting, initiation, and propagation of crack, (b) GTN simulation results showing high initial fracture toughness of EDM cut crack as compared to sharp crack front.

The J- Δa curve in the present study was generated using crack cut using EDM. The simulation has included crack tip radius of 0.125 mm. After successfully calibrating and validating the X70 GTN model parameter, sharp crack tip simulations were run. In the sharp crack tip SENB simulation a very small protrusion of 0.05 mm was given for the smooth fracture initiation. J- Δa curves were simulated for the SENB $a_0/W = 0.50$, and $a_0/W = 0.25$. Figure 5.48 (b) shows the simulated J- Δa results of SENB with EDM and sharp crack. J values at $\Delta a = 1$ mm are compared; $J_{EDM0.5} = 1360.5$, $J_{sharp0.5} = 1277.4$, $J_{EDM0.25} = 2073.8$, and $J_{sharp0.25} = 1732.4$ kJ/mm². The results suggest the crack tip acuity has more impact with lower constraints as compared to high constraint tests. The simulated J- Δa curve shows two regions 'A' and 'B', initial region 'A' shows variation whereas curve meets at region 'B'. Similar trends from experimental results were also observed by (Park et al., 2017). The results show that EDM cut SENB can be utilized for GTN parameter calibration; these simulation models can further be used to simulate the results of sharp crack SENB.