

## 2.1 NEED OF HSLA STEEL IN PIPELINE INDUSTRY

To provide higher atmospheric corrosion protection than ordinary steels, a wide variety of alloy steels have manufactured for enhanced mechanical properties known as HSLA steels, which frequently used as line pipe steels [John Piper, 2002]. Due to higher toughness and strength values, low alloy steels have become famous for different applications like oil and gas transmission line pipes, offshore oil drilling platforms, bridges, building construction, and pressure vessels [Nathan et al., 2015]. The exploitation of natural gas and crude oil in the offshore fields has accelerated the advancement of pipeline steels, which are highly efficient in working at high operating pressure and temperatures as low as  $-50^{\circ}$  F [Akao et al., 1985]. To operate in the harsh environment and to maintain sufficient toughness as well as durability pipe manufacturers developed new grades of HSLA pipeline steel by using modern methods. These new grades of pipeline steel consist of various micro-alloying components such as V, Ti, Nb, and a small amount of carbon and sulphur content. For strain-based applications, HSLA steels should have sufficient toughness and deformability. Thermomechanically controlled processing (TMCP), followed by Accelerated cooling (ACC) promotes fine-grained microstructure by hindering dislocation mobility and gives a right combination of toughness and strength. The microstructure developed by this method supports the ductile failure in low-temperature environments.

## 2.2. WELDABILITY OF PIPELINE STEEL

It is essential to identify the suitable joining procedure for the welding of pipeline steel as well as the performance of the welded joint and its ability to satisfy the design load requirements during pipeline transmission. The weldability of pipeline steel generally includes the fabrication conditions under which it welded and the strength of pipeline steel to be welded as well as to perform satisfactorily in service. Crack susceptibility or hardenability in the steel welds indicated by using carbon equivalent. During the welding of pipeline steel, the combined effect of all essential alloying elements on the microstructure (e.g., the formation of martensitic structure) can be estimated by carbon equivalent. The change in microstructure widely decides the properties of steel after welding. The lower value of carbon equivalent always preferred for good weldability. To specify the limit of carbon equivalent for API pipeline steel grades, the American Petroleum Institute [API, 2102 and IIW doc, 1967] and International Institute of Welding (IIW) has given two formulas for calculating carbon equivalent. Equation (2.1) & (2.2) shows the carbon equivalent method as per American petroleum institute specifications.

$$P_{cm} = \%C + \frac{\%Si}{30} + \left( \frac{\%Mn + \%Cr + \%Cu}{20} \right) + \frac{\%Ni}{60} + \frac{\%Mo}{15} + \frac{\%V}{10} + 5B \quad (2.1)$$

$$CE_{IIW} = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%Mo + \%V}{5} + \frac{\%Cu + \%Ni}{15} \quad (2.2)$$

As per the API specifications, if the carbon mass fraction is higher than 0.12%, then equation (2.1) is used, while if the carbon mass fraction is smaller than 0.12%, then equation (2.2) is used. Cooling rates, as well as thermal cycles of welding, also play an essential role in the microstructure alteration in addition to the alloying of the metal [API Energy, 2008].

### 2.3 PHYSICOCHEMICAL BEHAVIOUR OF SUBMERGED ARC WELDING FLUXES

The physicochemical behavior and chemical composition of a flux mixture depends on the minerals and have a significant effect on the depth of penetration. Alkaline and alkali oxides produce vapors that get more easily ionized and thus create a stable arc. Vapors produced by MnO, FeO, NiO, CuO, and TiO<sub>2</sub> have average ionization potential and have a small influence on the stability of arc. Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> also decrease arc stability. With low viscous flux, more heat transfer takes place [Singh et al., 2013, Olson et al., 1979 and Russanevitz et al., 1938]. Table 2.1 shows the effect of various flux elements on the physicochemical properties.

**Table 2.1:** Flux behaviour related with physicochemical properties [Singh et al, 2013, Olson et al., 1979]

<i>Physico-chemical behaviour</i>	<i>Flux behaviour</i>
Arc Stability	<ul style="list-style-type: none"> <li>a) Flux containing material of various ionization potentials can affect the arc stability. FeO and CaO are easily ionized and improve the arc stability.</li> <li>b) Alkali and alkaline metals generate vapors which are easily ionized, and stabilize the arc.</li> <li>c) MnO, NiO, CaO and TiO<sub>2</sub> similar ionization potential to that of iron and have little effect on arc stability.</li> </ul>
Viscosity	<ul style="list-style-type: none"> <li>a) For the production of acceptable welded joint the viscosity of the molten flux plays an important role.</li> <li>b) During the welding process, heat transfer rate, reaction rate and diffusion strongly rely on the viscosity of flux. Lower viscosity flux has higher bulk diffusion rate due to which higher reaction rate occurred at slag-metal interface.</li> <li>c) Too high viscous flux will not absorb or transport gases at the slag-metal interface resulting in pocking marks on the weld bead surface.</li> <li>d) In SAW the weld penetration is widely affected by slag viscosity. High slag viscosity favors high weld penetration. Too high viscosity of slag prevents the gaseous product to escape from the weld pool and cause porosity in the weld.</li> </ul>
Slag detachability	<ul style="list-style-type: none"> <li>a) Chemical and physical properties of the flux are related to the slag detachability. The phase transformation in slag during cooling and the difference between the thermal expansion coefficients of slag &amp; metal affects slag detachability.</li> <li>b) When the flux contains gases and fluorite, poor slag removal is observed. Slag with [Cr, Mn, Al<sub>2</sub>O<sub>3</sub>, Cordierite] and [Cr, MgO, MnO] type spinel phases are difficult to remove.</li> <li>c) Slag readily detaches from the weld deposit if SiO<sub>2</sub>, CaO, TiO<sub>2</sub> is present. The improvement in slag detachability was observed on addition of Al<sub>2</sub>O<sub>3</sub> in the flux.</li> </ul>
Capillarity	<ul style="list-style-type: none"> <li>a) Interfacial tensions between the weld metal and the molten flux depend upon the flux composition. Interfacial properties are widely affected by little variation in surface active elements.</li> <li>b) Weld pool morphology is also widely affected by slag metal reactions associated with interfacial tensions.</li> </ul>

Metallurgical properties of weld depend upon the various slag-metal reactions occurring during welding. The slag-metal reaction can be represented by equation 2.3.

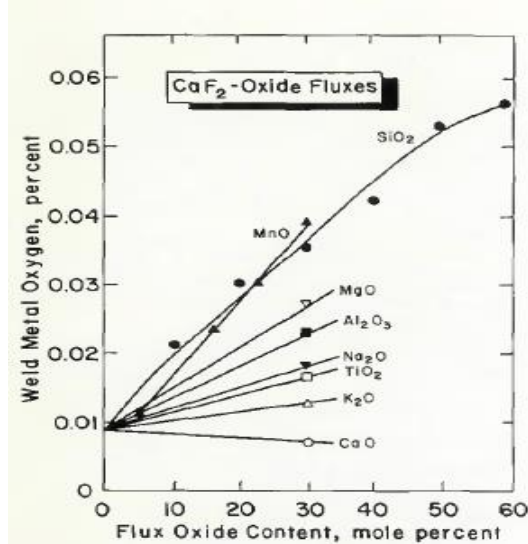


$M_xO_y$  is the metallic oxide in the slag, and M is the corresponding element dissolved in the molten metal. The slag-metal interactions must proceed thermodynamically to satisfy equilibrium conditions. The effect of different flux elements has reported on the weld metal composition such as silicon dioxide, manganese oxide, and iron oxide. The rise of manganese oxide in the flux leads to higher silicon dioxide and iron oxide concentration in the slag. Simultaneous Increase of silicon dioxide and manganese oxide will generally lead to an increase of manganese and silicon in the weld metal simultaneously [Palm, 1972]. Dissolved oxygen content has a disastrous effect on the impact strength. Several problems such as porosity, loss of fracture toughness, and reduced ductility, observed in weld metal due to the presence of high oxygen content. Available literature suggests that weld metal oxygen content significantly decreased with both increasing flux basicity and  $CaF_2$  content of the flux.  $CaF_2$  decreases the weld metal oxygen content due to the dilution of metal oxides rather than a direct chemical reaction. The effect of calcium fluoride in reducing the level of oxygen content is dependent upon the stability of the metal oxide present [Chai and Eagar, 1982; Davis et al., 1991].

Complex changes in the composition during submerged arc welding of C-Mn steel has related to the flux composition and weld metal inclusions as final reaction products in the arc plasma. Iron from steel (in the form of  $Fe^{2+}$  &  $Fe^{3+}$ ) and oxygen from flux ( $O^{2-}$ ) are the common ions present in the arc plasma. In arc plasma, other cations and anions present include  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Si^{4+}$ ,  $F^-$ ,  $SiO_3^{2-}$ ,  $SiO_4^{4-}$ . According to the reactivity, the fluoride ions will react rapidly as compared to the other anions. Oxygen and fluorine reactions generally occur at high temperatures in arc plasma. During these reactions, neutral compounds and reactive oxide radicals are formed involving other deoxidant elements. As per the solubility, these elements react further in the weld pool or slag. These elements absorbed by slag or may remain as inclusions in solidifying metal if they react in the weld pool. Flux elements like manganese, titanium, aluminum, sulphur, and silicon transferred from flux mixture to weld pool and some from the molten pool to slag, but transfer efficiency depends upon the type of anions present or reaction with silicate anions during slag-metal reactions [Davis et al., 1991]. [Kanjilal et al., 2007] observed that by developing quadratic models in terms of flux constituents with the help of a mixture design approach, the transfer of elements across the molten weld pool had predicted. For a  $CaO-MgO-CaF_2-Al_2O_3$  flux system, the submerged arc welding fluxes were prepared as per the extreme vertices algorithm of mixture experiments and using constant welding parameters the bead-on-plate weld deposits made. Experimental results show that individual, as well as binary flux mixture components, have a significant effect on the weld metal manganese, silicon, oxygen, and carbon contents. During the analysis of the experimental results, it observed that several properties of flux components such as oxygen potential, thermodynamic stability, and viscosity affect the transfer of oxygen. At constant welding parameters, the variation of transfer of elements across the weld pool is primarily due to the chemical reactions associated with submerged arc welding fluxes. Both electrochemical and thermochemical reaction mechanisms operate simultaneously in the element transfer of silicon, while manganese transfer is related to the electrochemical reaction as well as weld metal oxygen content in the molten weld pool.

[Chai et al., 1982] studied the stability of binary  $CaF_2$ -metal oxides in submerged arc welding. The oxides observed during the investigation include  $MnO$ ,  $MgO$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $K_2O$ ,  $Na_2O$ , and  $CaO$ . Results indicate that the stability of metal oxides during welding was not exactly similar to their thermodynamic stability. Some fluxes in arc plasma may dissociate into sub-oxides. Such oxides produce a high level of oxygen in the weld metal

than chemically stable oxide and result in reduced impact toughness of the weld metal. It found that  $\text{CaF}_2$  in the weld metal reduced the amount of oxygen by the dilution effect (dilution of metal oxides). In submerged arc welding, the addition of  $\text{FeO}$  (less than 10%),  $\text{MnO}$ , and  $\text{SiO}_2$  are the primary sources of oxygen contamination [Chai et al., 1982]. Calcite is the commonly used mineral which provides gaseous protection. Thermal decomposition of calcite takes place at  $950^\circ\text{C}$ , leading to the formation of  $\text{CaO}$  and  $\text{CO}_2$ , which further to decompose into carbon monoxide and atomic oxygen.  $\text{CaF}_2$  significantly increases the silicon content in the weld metal because it reduces the oxidizing potential for  $\text{SiO}_2$  by forming silicon fluoride by the reaction  $2\text{CaF}_2 + \text{SiO}_2 \rightarrow 2\text{CaO} + \text{SiF}_4$ . While silicon in the weld metal reduced with the addition of  $\text{MnO}$  in the flux due to oxidation of weld metal by the  $\text{MnO}$  and  $\text{Si}$  in the metal acts as deoxidizer [Chai and Eagar, 1982, Lau, et al., 1986]. Figure 2.1 shows the analysis of flux oxygen content present in the weld metal.



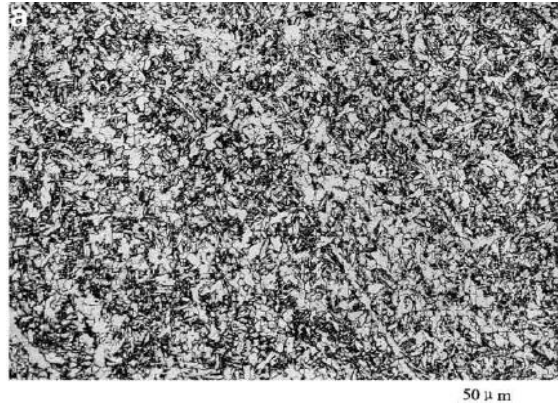
**Figure 2.1:** Weld metal oxygen analysis as a part of the percent metal oxide contained in the flux [Chai and Eagar, 1982]

## 2.4 EFFECT OF FLUX COMPOSITION ON MECHANICAL AND MICROSTRUCTURAL BEHAVIOUR OF PIPELINE STEEL WELDS

[Bang et al., 2009] observed the effect of flux composition on the tensile strength, impact toughness, and chemical composition of weld metal and interpreted it in terms of element transfer between slag and weld metal (i.e.,  $\Delta$  quantity) in SAW welding. The negative sign shows the transfer of elements from weld to slag, while a positive sign shows the transferring of elements from slag to the weld pool. During welding, carbon & manganese shows negative  $\Delta$  quantity indicating the transfer of elements from weld to slag. Depending upon the flux composition, the amount of transfer of elements may be different. Less negative  $\Delta$  carbon and  $\Delta$  manganese observed for more basic fluxes due to the reduction of oxygen content in the weld metal. With an increase in the basicity index of flux, the impact toughness increased due to the decrease in oxygen content in the weld metal. For long service life of weld joint, selection of suitable flux composition and compatible filler wire is essential. Growth of austenite grains is inhibited when  $\text{TiN}$  particles pin the prior austenite grain boundaries of the heat-affected zone (HAZ). Growth of proeutectoid ferrite suppressed when boron (B) particles segregate in the boundary of prior austenite grains. Weld metal toughness, as well as hardness, is high. The tensile strength of the weld joint is higher than that of base metal [Peng et al., 2001]. Available literature suggests the effect of basic coating mixture on the weld metal chemistry and mechanical behavior of dissimilar welds using extreme vertices approach.

Various coating mixture constituents indicate a different role in increasing or decreasing the mechanical properties. It observed that the increase in titanium oxide, silicon dioxide, and

calcium fluoride content of mixture tends to increase the tensile strength while a higher rise of SiO<sub>2</sub> indicates a decreasing effect on microhardness [Bhandari et al., 2016]. Some researchers investigated the effect of filler wire content on the mechanical and microstructure behavior of SAW welded API X65 steel. Polygonal ferrite, widmanstatten ferrite, acicular ferrite (Figure 2.2) and martensite-austenite (M/A) islands were observed in weld metal but acicular ferrite microstructure is more dominant in weld region. A combination of ferrite-bainite and M/A constituents found in the heat-affected zone (HAZ) specimens. Presence of more volume fraction of acicular ferrite in the microstructure results in higher mechanical properties. Weld specimen having a higher value of titanium and boron content promote the formation of acicular ferrite microstructure and improves tensile strength and impact toughness values [Beidokhti et al., 2015].



**Figure 2.2:** Acicular microstructure for API X65 fused metal [Beidokhti et al., 2015]

[Brijpal et al., 2016] conducted an experimental study to evaluate the effect of calcium fluoride (CaF<sub>2</sub>), iron-manganese (FeMn), and nickel oxide (NiO) additions on the mechanical properties of low carbon steel. CaF<sub>2</sub>, FeMn, and NiO elements added to the base fluxes (i.e., agglomerated fluxes were containing SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub>) in varying amounts (2-8 %). Mathematical models were developed using design experts and correlated with the nickel, manganese, and carbon transfer to the weld bead. It observed that the interaction of calcium fluoride and ferromanganese is significant for impact toughness while that of calcium fluoride & nickel oxide is significant for the hardness of weld. The optimum range of manganese and nickel content produces excellent mechanical properties. Low silicon (below optimum level) favors the development of carbon monoxide (CO), which produces porosity in the weld and decreases the toughness [Brijpal et al., 2016]. [Jindal et al., 2013] observed the role of flux mixture and Basicity Index (BI) on microhardness, tensile strength, and microstructure of the weld metal. With an increase in the basicity index, tensile strength increases while the opposite effect was observed in the case of microhardness. Ultimate tensile strength of weld increased with the rise of calcium oxide (CaO) in the flux, but, microhardness remains unaffected while the increase of silicon dioxide (SiO<sub>2</sub>) in the flux decreases the ultimate tensile strength. Weld metal exhibited fine grains of ferrite, i.e., acicular ferrite microstructure while heat-affected zone consists of coarse grains. [Vinod et al. 2010] investigated the influence of submerged arc agglomerated acidic fluxes on the mechanical properties of all weld mild steel specimens. Good bead appearance without any surface defects were observed with the use of laboratory prepared acidic fluxes. The weld made using laboratory prepared acidic fluxes were found to be radiographically sound. The mechanical properties, as well as weld chemical composition of all specimens, developed using acidic fluxes, are comparable with the mechanical and chemical composition of weld prepared using commercial acidic fluxes.

## **2.5 EFFECT OF WELDING PROCESS PARAMETERS ON MECHANICAL PROPERTIES AND CHEMICAL COMPOSITION OF STEEL WELDS**

Bead-on-plate weld deposits on low carbon steel plates were performed using the submerged arc welding process at different welding process parameters and flux compositions. Weld metal chemical composition is majorly affected by the polarity as compared to the other welding parameters. Weld metal phosphorous, as well as sulphur content, is affected by dilution of weld deposits while weld carbon content is influenced by welding speed through an oxidation reaction. It noticed that weld metal hardness and yield strength are mainly influenced by welding process parameters, whereas the impact toughness determined by flux mixture variables [Kanjilal et al., 2006]. [Sanjay et al., 2018] studied the role of different heat input (e.g., 0.3, 0.4 & 0.5 kJ/mm) on the mechanical & microstructural properties of 409L ferritic steel using two different filler wires. Heat input affects various properties such as microhardness, tensile, microstructure, and percentage dilution. Adequate mechanical properties observed at a heat input of 0.4 kJ/mm irrespective of filler wire used. In the submerged arc welding process, excessive heat produced due to which thermal cycle affects the base as well as weld metal cross-section geometric profiles. Penetration, weld reinforcement, and heat-affected zones are broadly affected by these weld thermal cycles. [Harendra et al., 2012] studied the effect of welding input parameters on the weld bead shape profiles in different zones of submerged arc weldments using statistical analysis. Depth of penetration is majorly affected by welding speed and current while bead width is significantly affected by welding voltage & speed as compared to other weldment characteristics.

[Jindal et al., 2014] observed the effect of welding process parameters on microhardness, hydrogen content, and weld bead profile during submerged arc welding of HSLA low-alloy steel. Various parameters such as dilution, weld bead form factor, microhardness, and diffusible hydrogen content were optimized using the desirability function approach. Multiple regression models have developed for different output responses in terms of welding parameters. It observed that welding current is the most significant welding process parameter in controlling all the responses. Dilution and diffusible hydrogen content affected by welding current while voltage, as well as welding speed, shows no effect on diffusible hydrogen content. Welding current shows significant antisnergistic effect on form factor and microhardness, while voltage gives a significant synergistic effect on all the output responses except microhardness. [Jindal et al., 2011] observed the effect of submerged arc welding parameters on weld metal transfer in SS316. At different welding parameters, the bead on plate weld deposit experimentation performed on SS316. It observed that with an increase in current, voltage, and speed, the Cr and Si content in the weld bead increases while Mn content decreases.

## **2.6 EFFECT OF SLAG-METAL REACTIONS IN SUBMERGED ARC WELDING**

[North et al., 1979] observed that oxygen content has a considerable effect on the impact behavior of weld metal. The impact behavior of welds decreased abruptly with high oxide inclusions content. Low oxygen fluxes produce acicular ferrite microstructure due to the presence of 300ppm oxygen ( $O_2$ ) content in the weld metal. To identify the significant factors which control the final oxygen level in the weld metal, it is desirable to access and evaluate various kinds of reactions taking place during welding. [Lau et al., 1986] studied the  $O_2$ , Al, Mn as well as inclusions content at three stages of welding conditions. It observed that wire, fluxes, and parent metal of known compositions equally take part in slag-metal reactions. It noticed that the major sources of oxygen absorption are electrode tip and droplet stage. To determine the composition of inclusions and the level of Al and Mn showed that the primary source of oxygen is the decomposition of flux. It implies that the maximum decomposition of flux components takes place within the arc column. Slag-metal reactions may or may not occur at the weld metal stage. It observed that fluxes containing MnO show maximum metal-slag reactions while MnO free fluxes did not show these reactions. At the

weld metal stage, the significant loss of metallic species, such as Al and oxygen, indicated the separation of oxidation products, which is the main factor for determining the final oxygen content. The metal droplet stage (>1400 ppm) and electrode tip are the major sources for oxygen absorption, while weld metal (<700 ppm) shows much lower oxygen content as compared to electrode tip & droplet stage. This concludes that the final oxygen level in the weld metal is widely dependent on the slag-metal reactions [Lau et al., 1986].

## **2.7 EFFECT OF MICRO-ALLOYING CONSTITUENTS ON MECHANICAL AND MICROSTRUCTURAL BEHAVIOUR OF WELD METAL**

[Beidokhti et al., 2009] investigated the effect of Ti addition on submerged arc weld metal microstructure of API 5L-X70 steel. The additions of titanium in the range of 0.02-0.05% improve the mechanical properties. Further addition of titanium content, microstructure changes from a mixture of acicular ferrite, grain-boundary ferrite, and widmanstatten ferrite to a mixture of acicular ferrite, grain boundary ferrite, bainite with the inclusion of martensite-austenite constituents in the weld metal. The impact behavior of the weld metal enhanced by the addition of Ti, but a higher increase in the Ti results in the development of quasi-cleavage fracture mode from earlier dimple ductile mode. [Trindade et al., 2007] observed the influence of Ni content (0.50 wt. %-3.11 wt. %) on the toughness and microstructure of C-Mn weld metal obtained during the submerged arc welding process. [North et al., 1979] studied that various micro-alloying addition was influencing the impact properties of C-MnCb and C-Mn welds. In Multi-pass welds, the addition of aluminum in C-Mn deposits was beneficial to improve the impact toughness but was not useful in the case of C-MnCb welds. The influence of Mn, Si, Al, or Mg on the impact behavior of C-Mn and C-MnCb welds depends upon the cooling rate after welding. At a high cooling rate, notch toughness value observed to be low as compared to that observed during a lower cooling rate. Titanium and vanadium addition in low oxygen C-Mn and C-MnCb welds promote acicular ferrite microstructure, but zirconium and aluminum do not develop the acicular ferrite microstructure. [Yoshino et al., 1979] studied the effect of niobium micro-alloying element to improve the low-temperature notch toughness and strength in pipeline seam welds. It observed that a higher level of niobium (>0.03%) in the weld metal is critical to impact toughness because of the precipitation of niobium carbo-nitrides. Different methods suggested achieving a high value of toughness in the weld metal. These include:

- (a) Basic welding flux should be used rather than acidic flux to limit the oxygen absorption into the weld metals,
- (b) Weld metal-carbon content should be less than or equal to 0.07%.
- (c) Nickel & Molybdenum alloying elements should add in the weld metal. It suppresses the proeutectoid ferrite and upper bainite and favors acicular ferrite microstructure precipitation.

[Terashima et al., 1984] studied the effect of aluminum in Carbon-Manganese-Niobium steels on the weld metal toughness and microstructure during single-pass submerged arc welding. The study involved the use of welding wire (consisting of 0.5% Molybdenum and 1.5% Manganese), two types of basic fluxes, and calcium-silicate fused fluxes. Si-killed, semi-killed, and Al-treated steel plates used for the experimentation. By using basic agglomerated fluxes, there is a pronounced change in the weld metal notch toughness observed. The measured change in the impact behavior directly related to the noticeable changes in the microstructure. Increasing the aluminum content (0.007-0.060%) in the weld metal (made of 121 flux) results in a continuous decrease in acicular ferrite content and toughness. Table 2.2 shows the effect of various micro-alloying elements on the microstructure of Carbon-Manganese-Columbium steel weld deposits.

**Table 2.2:** Effect of Ti, Al, Mn, Zr and V on microstructure Carbon-Manganese-Columbium deposits [North et al., 1979]

Flux element	Flux type	Flux content	O <sub>2</sub> content	Microstructure
Mn	CMnCb	Increased	increased	Did not form Acicular ferrite
Ti	CMnCb	Increased	Lower	Acicular ferrite +Proeutectoid ferrite
Al	CMnCb	Increased	increased	Bainitic structure
Zr	CMnCb	Increased (upto 1.4 %)	Lower	Did not form Acicular ferrite
V	CMnCb	Increased	< 200ppm	Acicular ferrite

[Jorge et al., 2001] studied the effect of varying chromium content (0-3.8%) in submerged arc welding single-pass welds. The relation between toughness and microstructure of weld deposits was observed. The addition of chromium in weld metal promotes the development of acicular ferrite; however, it reduces the impact toughness value. An increase in the carbon content reduces impact toughness value due to the formation of martensite/austenite constituent. Acicular ferrite phase formed in the microstructure, at lower silicon content, i.e., 0.03-0.26 wt-%, and it improves the toughness value. A higher silicon content (0.42 to 0.95 wt-%), the acicular ferrite was not precipitated [Beidokhti et al., 2015]. Available literature reveals that the volume of proeutectoid ferrite is reduced with the addition of niobium (up to 0.03 %) and promotes acicular ferrite in C-Mn weld metal. The effect of Nb on proeutectoid ferrite reduced when niobium added with 0.3% Mo. Mo decrease the dislocation density of Nb-bearing weld metal. Strength and toughness properties are functions of carbon (C), Columbium (Cb), and vanadium (V). Table 2.3 shows the effect of various micro-alloying elements on the mechanical and microstructural behavior of pipeline steel welds [Yoshino et al., 1979; Signes et al., 1979].

**Table 2.3:** Impact of micro-alloying components on hardness, microstructure and notch toughness of pipeline weld [Y. Yoshino et al., 1979]

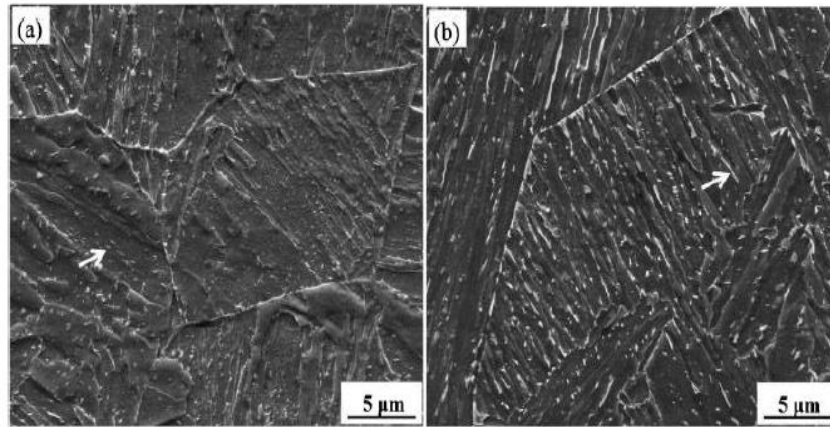
Micro-alloying elements	Notch toughness	Hardness	Microstructure	Dislocation density
Nb (upto 0.03 %)	Reduced	Increased	Acicular ferrite	High
Nb + 0.3% Mo	Moderate	Increased more	_____	Low
Mo (upto 0.35%)	Increased	Lower	Acicular ferrite	High
Ni	No significant effect	_____	_____	High
Ni + Nb (0.07%)	Lower	Increased	Acicular ferrite	High
Al (Acid flux)	Increased (Because of deoxidizing action of Al with acid flux)	_____	Fine	_____



Al (Basic flux)	Decreased (Al remain dissolved in weld metal)	_____	Coarse	_____
Ti	Increased	Increased	Coarse	_____
C (Acid flux) (Basic flux)	Increased More Increase			

## 2.8 EFFECT OF COOLING RATE ON THE MECHANICAL AND MICROSTRUCTURE BEHAVIOUR OF PIPELINE STEEL & PIPELINE WELD

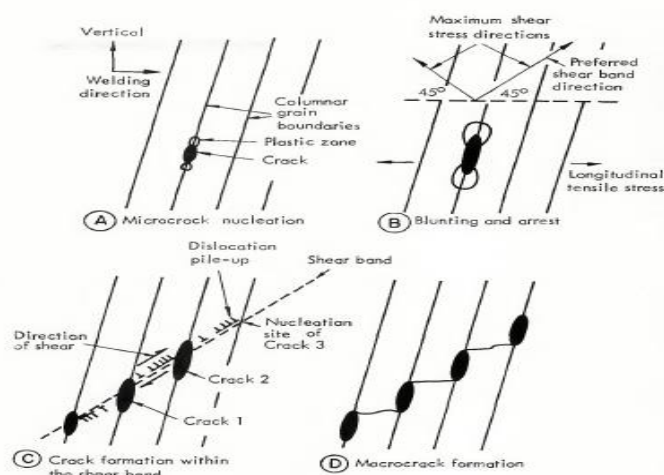
[Harish et al., 2018] investigated the effect of cooling rate on microhardness, impact toughness and microstructure of heat-affected zone of submerged arc welding (SAW) weldment of SA 516 pipeline grade steel. Variation in base plate thickness affects the cooling rate due to changes in heat input. Experimental results showed that there is a loss of acicular ferrite microstructure due to grain coarsening and further reduction of impact toughness when there is an accumulation of heat across the thin plate section. Faster cooling takes place in a higher thickness direction due to the heat sink, which results in a higher percentage of acicular ferrite with fine grains and higher hardness value. [Yan et al., 2014], observed that rapid cooling, followed by considerable heat input during the submerged arc welding process decreases the size of HAZ and coarse-grained region in the E690 offshore steel. The optimum decrease in austenite grain size (from 40 to 25 $\mu$ m) with smaller content of remaining martensite-austenite (M/A) constituent (5.36 in case of rapid cooling and 11.6 in case of traditional cooled ones) leads to better improvement in the low-temperature impact behavior of test specimens. Figure 2.3 shows the micrographs of martensite-austenite (M/A) constituents in the coarse-grained heat-affected zone. Available literature suggests that for better performance of pipeline steel in the severe service environment, the mechanical properties of weld metal and heat-affected zone (HAZ) play an essential role. Microstructure plays a critical role in improving the strength without significant loss in impact toughness. High heat input, favors the formation of coarse grain microstructure and martensite-austenite (M/A) constituent in the heat-affected zone (HAZ). M/A (Martensite-austenite) constituent and grain coarsening present in the heat-affected zone (HAZ) structure are the main reasons for the toughness deterioration in the weld area. A fine microstructure and reduced formation of martensite-austenite constituents will lead to improving the HAZ toughness in X70 and X80 pipeline steels. It observed that during welding processes, excessive heat produced at the weld - metal interface and near the heat-affected zone (HAZ). The extreme heat of welding results in thermal cycles that lead to interfacial coarse grain regions, which form local brittle zones in the heat-affected zone. As heat input increases and cooling rate decreases, the microstructure of heat affected zone changes from martensite to lower bainite, upper bainite, and then to ferrite and pearlite. The presence of hard martensite/austenite phase in the microstructure deteriorates the impact toughness [Liu et al., 2013]. [Kanwer et al., 2019] investigated the impact toughness & microstructure of various reheated coarse-grained heat-affected zones, and during the study, they found that X65 has higher impact toughness as compared to the X80 due to soft ferrite and pearlite phases in the microstructure.



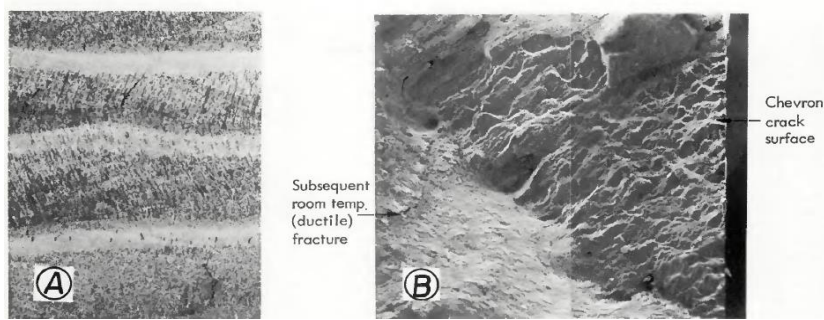
**Figure 2.3:** Shows the high magnification micrographs of MA elements (arrowed) in coarse grained HAZ, (a) rapid cooling (b) conventional cooling [Yan et al., 2104].

## 2.9 EFFECT OF SUBMERGED ARC WELDING FLUXES ON DIFFUSIBLE HYDROGEN CONTENT AND HYDROGEN INDUCED CRACKING IN WELDS

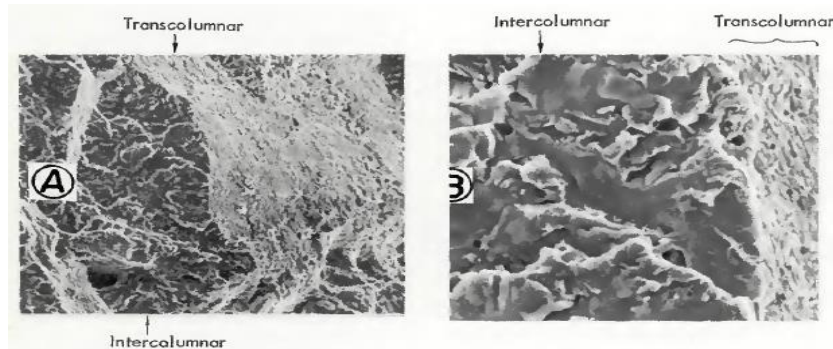
Among all basic oxides, it is calcium oxide that has a more significant ability to absorb and fix the water in the structure. It has excellent capability of reducing hydrogen and oxygen contents in the molten arc. Higher the carbonate fraction, higher is the basicity of slag, and lower is the hydrogen content in a weld. The suitable fluidity of molten slag and the reduction in diffusive hydrogen content were obtained by adding flux constituents containing fluoride ions [Plessis et al., 2007]. Hydrogen embrittlement is generally more susceptible to high strength weld metals, which causes metallurgical changes during the solidification. Chevron cracking observed at high hydrogen level and electron fractography demonstrated that both the transcolumnar and intercolumnar crack components formed in the weld metal. [Vishal et al., 2019] investigated the degradation of fatigue & tensile properties of X65 pipeline steel due to hydrogen blister formation. X65 steel specimens were charged at the rate of 20mA/cm<sup>2</sup> in the hydrogen environment to study the hydrogen-induced cracking and blister formation. [Allen et al., 1982] studied the performance of laboratory and industrial cracks using various modern microscopy techniques. Figure 2.4 shows the crack mechanism formed during chevron cracking. Figure 2.5-2.7 shows the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of various types of cracks developed during the chevron cracking mechanism. Table 2.4 shows the different cracks observed during submerged arc welds.



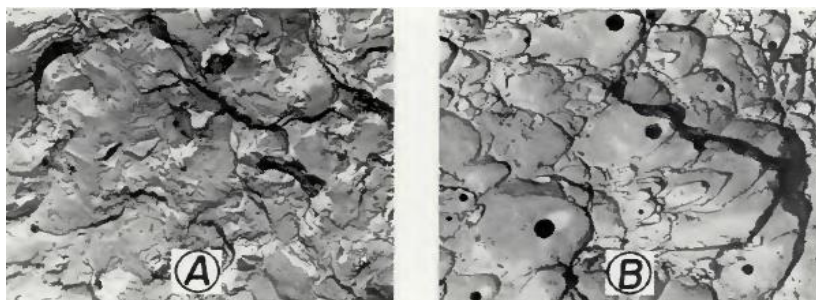
**Figure 2.4:** Mechanism of crack formation associated with dislocation shear bands: A- micro-crack nucleation B- blunting and arrest; C- crack formation within the shear bands; D- macro-crack formation. [Allen et al., 1992]



**Figure 2.5:** Example of chevron cracking: A- Cracking in a vertical longitudinal section; B- SEM image of crack surface after breaking at room temperature [Allen et al., 1992]



**Figure 2.6:** Example of chevron cracking: Fracture morphologies in the as-weld regions by using scanning electron microscope (SEM) [Allen et al., 1992]



**Figure 2.7:** Fracture morphologies in the as-weld regions by using transmission electron microscope (TEM) (a) inter-columnar cleavage; (b) trans-columnar dimples [Allen et al., 1992]

**Table 2.4:** Cracks formation observed during submerged arc welds at high temperature [Allen et al., 1992]

Type of Crack Observed	Optical metallography	SEM analysis	TEM analysis
Inter-columnar crack	Shows appreciable width of crack	Showed ductile shear dimples with no evidence of thermal Faceting.	Inter-columnar fracture surfaces were generally smooth and featureless but showed evidence of thermal faceting and grain boundary grooving.
Trans-columnar cracks	Always shows thin width of crack		

## 2.10 LITERATURE ON FLUX FORMULATION DESIGN

Available literature suggested a method to design the flux formulations from different constituents such as  $\text{CaF}_2$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{MnO}$ , and  $\text{Al}_2\text{O}_3$ . The mixture design approach of the design of experiments was used to design flux compositions. Suitable results characterized by an average ratio of  $\text{MnO}/\text{SiO}_2 = 1.42$  [Crespo et al., 2007]. [Adeyeye and Oyawale 2008] studied the mathematical tool for welding flux design. Authors suggested that for flux designing mixture design approach is more suitable as compared to the factorial design where only proportions matter and not the amounts. The extreme vertices approach of mixture design is more suitable for flux designing as compared to other techniques. The basic requirement for designing flux compositions is that the melting temperature of flux constituents should be lower than that of base metal or filler material, and it should remain in liquid form after solidification of the weld metal [Bhandari et al., 2012]. [Jindal et al., 2013] suggested submerged arc welding flux design using an extreme vertices approach for HSLA steel. Regression models in terms of flux ingredients developed for percentage elongation, tensile strength, and impact toughness. [Adeyeye and Oyawale 2009] suggested a new approach for the optimization of fused metal properties using flux constituents. In previous literature by [Kanjalal et al., 2006 and Kanjalal et al., 2007], single-objective optimization responses of flux mixture were utilized. A previous study reveals that on the addition of iron powder into agglomerated flux, the weld performance improves at optimum welding parameters. Welding efficiency and depth of penetration improved with the addition of iron powder [Sakaguchi et al., 1994]. Liquid sodium or potassium silicates are the most common agglomeration agents used for granulation of fluxes, which provides smooth and better arc stability during welding. Arc stability and smooth arc initiation depend upon the transfer of flux ingredients in the arc plasma during welding. The authors used the  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{CaO}$  ternary system to formulate agglomerated fluxes [Quintana et al., 2003]. [Datta et al., 2008] solved multi-objective optimization problem by using the Taguchi approach and grey relational analysis for the submerged arc welding process. During experimentation, unmelted fresh flux mixed with slag in varying proportions. The percentage proportion of slag and flux, flux basicity, and welding current is taken as process variables. For achieving favorable weld quality in terms of bead morphology, only a 10% slag-mix should use. Paniagua-Mercado et al., (2003) studied the thermo-chemical behavior of different ions formed during the agglomeration of fluxes. The authors observed the various phases using the X-ray diffraction technique. Three flux formulations developed, and different characterizations such as chemical analysis using XRF, thermal behavior using differential thermal analysis (DTA) were carried out. [Jindal et al., 2013] observed the chemical composition of carbon, silicon, manganese, sulphur, and phosphorous in the weld metal. Constrained mixture design was used to formulate the fluxes and to study the effect of flux constituents on weld metal composition. Experimental results reveal that among all the individual flux components,  $\text{CaF}_2$  and  $\text{Al}_2\text{O}_3$  are the most significant flux constituents. Binary mixture components such as  $\text{CaO}$ - $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ - $\text{MgO}$  are the most effective in changing the weld metal composition. [Kozyrev et al., 2013] studied that during submerged arc welding of low-alloy steel, the oxygen content of weld metal reduced by adding additions to the flux. The mechanical properties such as impact toughness of welded joints increased at sub-zero temperature due to the reduction of non-metallic inclusions in the weld metal. Effective deoxidation of weld metal observed with the use of these additions as compared to the Si and Mn reduction processes. [Kozyrev et al., 2015] compared the effect of carbon-fluorine additions to the AN-67, AN-60, and OK 10.71 fluxes in submerged arc welding. Results reveal that the addition of carbonaceous components in welding fluxes reduces the non-metallic oxide inclusions content and improves the mechanical properties of weld joints. [Kozyrev et al., 2017] studied the effect of carbon-fluorine additions to the AN-348, AN-60, and AN-67 fluxes during submerged arc welding of 09G2S steel. Thermodynamic mobility of reactions during slag-metal interactions, reduction agents in liquid melts-oxide melts, and the reduction properties of carbon with other elements were evaluated using carbon-containing additions for submerged arc welding fluxes. High reduction properties (at temperature 1950-2200 K) observed when carbon added to the composition, and it exerts a strong effect on the

oxygen content of the system. Weld metal-carbon percentage remained at the same level of base metal percentage when carbon-fluorine additions used for submerged arc welding fluxes. [Paniagua-Mercado et al., 2009] investigated the effect of titanium dioxide containing fluxes on the microstructural and mechanical properties in SAW steel welds. Four fluxes were having different titanium dioxide percentages (nine, twelve, fifteen, and eighteen weight percentage of titanium) used with low carbon electrode filler wire. For each flux acicular ferrite and equiaxed ferrite, the microstructure observed in the weld metal. With an increase in the titanium dioxide content, there is an increase in the percentage of acicular ferrite content in the microstructure. It improves the weld metal toughness & ductility. [Paniagua-Mercado et al., 2005] studied the role of the chemical composition of flux on the tensile properties and microstructure of submerged arc welds. Three flux compositions and one commercial flux composition used with low-carbon filler wire. Weld joint prepared from the flux composition having a higher content of titanium dioxide exhibits acicular ferrite microstructure. An increase in titanium dioxide content in the weld metal increases the yield as well as ultimate tensile strength. A decrease in the inclusion percentage in the welds increases percentage elongation. [Fox et al., 1996] studied the effect of flux basicity index on the mechanical properties and microstructural behavior of SAW weld metal of HY-100 steel. During the experimental analysis, it was observed that total oxygen content (0.034 to 0.027 wt %) of weld metal decreased with an increase in flux basicity from 2.5 to 3.0. Due to the decrease in the weld metal oxygen content, there is an increase in the size of non-metallic inclusion, which increases the possibility of acicular ferrite formation. The formation of acicular ferrite microstructure tends to increase the strength as well as the toughness of the weld metal. The experimental result suggests that careful control of the chemical composition of both filler wire and flux plays an important role in improving the strength & toughness of the weld metal during SAW welding of HY-100 steel. Jindal et al., (2013) developed the submerged arc agglomerated fluxes for welding of high strength low alloy steel. Different regression models of ultimate tensile strength, impact strength, and microhardness developed in terms of flux mixture constituents. Individual flux component such as calcium oxide tends to decrease the impact toughness value while binary mixture components  $\text{CaF}_2$ . $\text{CaO}$  &  $\text{MgO}$ . $\text{CaO}$  gives a positive effect on weld metal tensile strength. [Jindal et al., 2015] observed the element transfer of flux constituents from slag into weld metal and from weld metal into slag during high-strength low alloy steel welds. The element transfer of flux constituents such as carbon, silicon, manganese, sulphur and phosphorous from slag into weld metal and vice versa was studied using formulated fluxes. The experimental result shows that among all the individual flux components, calcium oxide and aluminum oxide are the most significant flux constituents. A significant effect on element transfer and microhardness value observed for the  $\text{CaO}$ . $\text{Al}_2\text{O}_3$  &  $\text{CaO}$ . $\text{MgO}$  binary mixture components. [Masao et al., 1995] observed the effect of SAW flux composition on the weldment performance. Five formulations of  $\text{SiO}_2$ - $\text{CaO}$ - $\text{MnO}$  fluxes were prepared using local raw material. The performance of the laboratory prepared fluxes was evaluated and compared with the two commercial fluxes. The experimental result shows that locally produced fluxes provide good slag detachability, high arc stability, lower hydrogen content, and reasonable penetration. [Kettel W. K., 1993] studied the effect of submerged arc weldments on the mechanical properties and microstructural behavior of HY-100 steel. Commercial flux used for submerged arc welding of HY-100 steel. Microstructure analysis of weldments was used to find the toughness variation in the weld metal. It observed that weld metal toughness and strength widely affected by the flux basicity index. Highly basic flux results in larger weld metal toughness and strength due to the subsequent non-metallic inclusion formation. A larger volume percentage of inclusion increases the nucleation of acicular ferrite, which is found to be beneficial for increasing the toughness value. Inclusion characterization revealed that the role of the flux in alloy had a more promising effect on the toughness and strength than the presence of some specific inclusions. [Burck et al., 1990] observed the effect of calcium fluoride, iron oxide, and calcium oxide on weld metal chemical composition for manganese-silicate flux system. Weld metal chemistry of low-carbon steel welds and AISI 4340 steel welds were studied. Thermodynamic data was used to study the effect of these additions during element transfer from slag to weld metal and from weld metal to

slag. In 1010 steel welds, the carbon-oxygen partition appears to be controlled by carbon-monoxide (CO) reaction, while for SiO<sub>2</sub>-CaF<sub>2</sub>-MnO flux system, the manganese level remains constant.

## 2.11 IDENTIFICATION OF GAPS FROM LITERATURE

A review of the research literature reveals that following aspects remains unexplored in the research related to submerged arc welding fluxes:

- Literature is available on the effect of submerged arc welding parameters on mechanical properties of weld metal but very limited literature is available on the physicochemical behavior of submerged arc fluxes.
- Limited literature is available on the suitable selection of SAW basicity index range for welding of API pipeline steels.
- Limited work has been reported on the effect of SAW basicity index on density, thermal conductivity, change in enthalpy, percentage weight change, slag detachability, diffusible hydrogen content, and corrosion behavior of API grade pipeline steel.
- No attempt has been made to correlate the regression models of physicochemical and thermophysical properties of submerged arc fluxes for welding of pipeline steel.
- No attempt has been made to explore the effect of physicochemical behavior of submerged arc fluxes on mechanical & microstructural properties of pipeline steel.
- Limited work has been reported on the SAW weldment corrosion as well as hydrogen induced cracking (HIC) study of pipeline steel using basic, rutile basic and rutile acidic flux systems.
- Limited work has been reported to explore the effect of different heat treatment conditions on pipeline steel in various exposing environments such as fresh water, sea water, sodium thiosulphate (pH=3 & 5) solution.