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EFFECT OF PHYSICO-CHEMICAL PROPERTIES OF SUBMERGED ARC WELDING FLUXES ON PIPELINE STEEL – A BRIEF REVIEW

Pipeline welding is an integral part of oil and gas exploration industries. Often the welded joint failures were due to lack of weld quality, improper heat treatment and even poor workmanship. Further, the use of new material in pipeline industry puts focus on a better understanding of qualifying requirements of welding for reducing the failures in future. This necessitates the need for development and design of suitable welding fluxes for joining these materials. In this paper an attempt is made to study the effects of submerged arc welding fluxes on weldability as well as structural integrity issues in pipeline steels. Physicochemical and thermophysical properties of submerged arc fluxes widely affects the mechanical behaviour of pipeline steels. This paper presents an overview of the role of welding parameters, flux composition, cooling rate, slag behaviour and physicochemical properties of slag on final welded joint properties such as tensile strength, impact toughness etc. during submerged arc welding.

Keywords: Pipeline steel; submerged arc welding (SAW) fluxes; physico-chemical properties; structural integrity issue; mechanical properties

1. Introduction

In 70s and 80s due to the advancement in the steel manufacturing processes, such as ladle processing for alloy additions, basic oxygen furnace production, continuous slab casting and vacuum degassing pushed pipe manufacturer to produce stronger and technically challenging steels [1]. The line pipe grade most commonly used evolved rapidly from X52 to X60 and then X65 to X70 through 1990 with these technologies. In 1993, a new grade (X80) to the pipeline family came with parallel development in X70. The need for the development of X70 and X80 grade was that alloy system used for X65 production consisting of titanium stabilised carbon manganese steel strengthened with niobium and vanadium which had a limited ability to be extended to higher strengths [2]. Carbon equivalent approaches an unacceptable level as strength increases to the addition of higher alloy content. For this, vanadium was replaced by molybdenum, strong carbide former and the very effective strengthening agent was added. The high effectiveness of molybdenum along with the use of niobium allows for strong alloy [3]. Fig. 1 represents development of various grades of pipeline steel with passage of time.

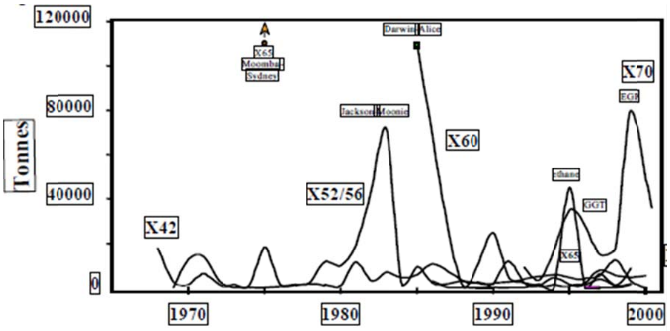

Fig 1. Different pipeline steel grades [2]

1.1. Need of HSLA steel in Pipeline industry

To provide higher atmospheric corrosion protection than normal steels, a wide variety of low alloy steels manufactured for enhancing mechanical properties known as HSLA steels which are frequently used as line pipe steels [4]. HSLA steels are extensively used in many applications. Due to higher toughness and strength values, low alloy steels to became popular with different applications like oil and gas transmission line pipes, offshore oil

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drilling platforms, bridges, building construction and pressure vessels [5]. 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° F [6-7].

1.2. Properties of steel designed to be used for gas pipeline construction

The compositions of various API steel grades have been shown in TABLE 1 [8-11]. In order to enhance the steel strength the different processes should be employed for pipeline materials like alloy addition such as Mn, Si and B form a solid solution with iron, strengthening the ferrite. Bainitic and martensitic phase transformation also improve the strength of HSLA pipeline steels [3,6]. TABLE 2 represents the mechanical behaviour of different API steel grades.

2. Fabrication Issues

At an early stage in development of line pipe steel many basic decisions were made- those include the selection of line pipe material, joining of line pipe steel and design considerations. By analyzing and to identify the processes associated with high pressure transmission pipeline these issues can be addressed. Loading conditions almost different to every weld on an offshore pipeline constructed, so the designer should be capable of identifying the locations where axial loading is higher such as landslip area, area subjected to settlement and area subjected to thermal stresses and bending [12]. In pipe manufacturing, to reduce the required pipe wall thickness and optimize pipeline construction costs high grade steels developed. Standard pipeline construction practices were followed during pipeline construction like field bending, pipe handling and hydrostatic testing and there was no problem encountered during this testing. But it was only for welding and inspection special procedure need to be followed. For line pipe joining MMA and GMA welding were used and initially high repair rates occurred, i.e. relatively half percentage of welds requiring improvement. The defects experienced were mainly loss of heating; the total length of maintenance in comparison to total welds length below that experienced in other line pipe activities. Defect rates were reduced drastically with increase experience of full pulsed and automated processes like pulsed GMA welding and submerged arc welding (SAW). Large diameter pipeline projects (e.g. Ruhrgas in Germany, Nova Corporation and TransCanada Pipelines) MMA welding and GMA welding process is generally used and weldability parameters were calculated in accordance with Welding Institute of Canada (WIC) to determine to preheat requirements for the use of a cellulosic root bead (E410 10 AWS 6010). For cellulosic welding the standard preheats temperature of 100°C was specified by Nova Corporation [13]. TABLE 3 shows the effect of various welding processes on the productivity as wel as strength of welded joint.

In 1950 and 1960, the hot rollers and normalizing of steel plate were used to manufacture large diameter line pipes with excellent material characteristics. With the passage of timing the demand of line pipes in offshore transmission has increased and with the advent in technology to manufacture pipeline steel also changed. Thermomechanical rolling to create the fine grain structure of improved toughness and yield strength of the material and this enabled manufacturing of higher grade steel such as X70 [14]. With advent of X70 grade to steel it was found that the structural transformation necessary to further increase the yield strength which could be achieved through accelerated cooling followed by water quenching immediately after the final stage of the rolling process. This transformation produced an extremely fine grain microstructure with high toughness. It is reported that the carbon content in line pipe to promote the sensitivity towards hydrogen cracking, due to this X80 steel is more susceptible to hydrogen cracking because carbon equivalent of X80 is higher as compared to lower grade steels. Adequate welded joint is required to fulfil the specified strength of line pipe steel as specified during the manufacturing process. To solve this problem, combined electrode manual welding technique was used. For large practical applications this combined electrode manual welding technique frequently utlilized in the industry [15-17].

During submerged arc welding, melting of both parent metal as well as filler wire take place under the blanket of agglomerated fluxes. Oxidation as well as contamination of the weld pool has been protected by the outer layer of the flux formed in

TABLE 1

Chemical analysis for various API grade steels

API	Si	C	Mn	S	Al	P	V	Ti	Cu	Cr	Ni	Mo	Nb	N	CE_{IIW}
X80	0.31	0.56	1.90	0.0015	0.029	0.011	—	0.018	0.044	—	0.221	0.213	0.046	0.0044	0.43
X70	0.18	0.06	1.55	—	—	—	—	0.017	—	0.02	—	—	0.055	0.007	0.42
X60	0.2	0.7	1.5	.01	.035	.014	.04	.01	.17	.01	.09	.01	.03	—	0.41

TABLE 2

Tensile strength and yield strength behaviour for various pipeline grade steels

API code	Y_{st} (MPa)		T_{st} (MPa)	
	Lower value	Higer value	Lower value	Higer value
X80	555	705	625	825
X70	485	635	570	760
X65	450	600	535	760
X60	415	565	520	760
X56	390	545	490	760
X52	360	530	460	760

TABLE 3

Effect of different welding processes/consumables on productivity and strength of welded joint

Type of Process	Pass applied	Type of Electrode used	Weld position	Productivity	Joint strength
Cellulosic/low hydrogen	Root and Hot Fill and Cap	E480 10 (AWS 7010) E690 18 (AWS 10018)	Down hill Up hill	Very low	Poor
Cellulosic/low hydrogen	Root and Hot Fill and Cap	E550 10 (AWS 8010) E620 10 (AWS 9010)	Down hill Down hill	Good	Marginal
Cellulosic/low hydrogen	Root and Hot Fill and Cap	E480 10 (AWS 7010) E620 18 (AWS 9018)	Down hill Down hill	Good	Good with low susceptibility to hydrogen cracking of cracks free from undercutting
GMAW	Root and Hot Fill and Cap			Higher than MMAW	Reduced susceptibility to hydrogen cracking
Pulsed-GMAW	Not suitable for root pass due to the presence of magnetism in pipe			Higher	Lower weld defects with increased productivity

the form of slag on the weld pool. Due to this total heat input is fully concentrated into the welded joint. Flux not only protect the weld pool but it also act as a cleanising agent in submerged arc welding process. Due to this reason submerged arc welding (SAW) process is mostly used as compared to other arc welding processes [18-19].

2.1. Role of submerged arc fluxes in weldability of pipeline steel

In submerged arc welding, the various physicochemical and thermomechanical interactions exist in the weld pool during decomposition of metallic constituents to the weld. During welding, different metallic oxides dissociates in the arc region and promote the phase transformation [20]. In submerged arc welding, accicular ferrite phase is formed due to the interaction of various oxides in the weld pool at high temperature and this particular phase is responsible for enhancing the impact strength of SAW weldments. There is much similarity in the behaviour of submerged arc welding (SAW) fluxes with that of coating mixture used in covered electrodes in case of MMA welding. In both cases, the role of the mineral mixture is to protect the welded joint from welding defects and atmospheric gases because there is transferring of different mineral constituents in the weld pool during slag-metal and gas-metal interactions [21-24]. The various important constituents which affect the weld metal are silicon, manganese, carbon and iron. An increase in SiO_2/MnO gives rise to a Manganese + Silicon amount of weld while diffused oxygen content also increased at the same time. The increase in manganese and silicon amount in the wire give rise to increase of Manganese + Silicon, but the oxygen is reduced at the same in the weld metal [25]. Calcite is the most commonly used mineral that provides gaseous protection. Thermal disintegration of calcite occur at 950°C leading to the formation of CaO and CO_2, which further to decompose into carbon monoxide and atomic oxygen. CaF_2 significantly increases the weld metal, silicon content because it reduces the oxidizing potential for SiO_2 by forming silicon fluoride by the reaction $2CaF_2 + SiO_2 \rightarrow 2CaO + SiF_4$ while silicon in the weld metal strongly reduced with the addition of MnO in the flux due to oxidation of weld metal by the MnO and Si in the metal act as deoxidizer [26].

2.2. Effect of Flux/wire composition in submerged arc welding

Bang et al. observe the effects of different flux compositions on the element transfer and mechanical behaviour of weld metal in submerged arc welding (SAW) by using different size metal-cored wires. Change in element transfer was observed in terms of chemical composition and mechanical properties by seeing the effect of the flux-wire combination. The negative sign shows the transfer of elements from weld slag while positive sign shows transferring of elements from slag to weld pool [27]. Peng et al. studied the effect of the high persistent ferrite wire for the submerged arc welding of pipeline steel. For better service life of line pipe steel it is essential to use submerged arc welding (SAW) flux having higher efficiency. Uniformly distributed and fine dispersed molecules in the weld metal can support the development of acicular ferrite [28]. Jindal et al. studied the development, design and increase to flux mixture for SAW welding of HSLA steel. Constrained mixture method and extreme vertices methodology were used to design agglomerated fluxes for finding the effect of flux mixture constituents on different properties like tensile strength, impact behaviour and hardness of the fused metal [29]. Bhandari et al. observe the effect of rutile basic coating mixture of the weld metal chemistry and mechanical behaviour of dissimilar welds using extreme vertices approach. Various coating mixture constituents indicate a different role in increasing or decreasing the mechanical properties [30]. Brijpal et al. suggest the competent range of manganese and nickel contents that produces excellent mechanical properties. High weld manganese and nickel amount favors micro segregation leading to decrease of acicular ferrite and impact value. Low silicon (below optimum level) favors development of CO, which produces porosity in the weld and decreases toughness value [31]. Ajay et al. reveal that hardness rises with the weight% of flux elements i.e., CaF_2, MnO, NiO, MgO and Fe-Cr. CaF_2 and MgO widely change the hardness value, as CaF_2 affects less on hardness because it reduced oxygen level due to interaction with SiO_2 and non reacting nature of metal oxide [32]. Jindal et al. observe the role of flux mixture and BI on microhardness, tensile strength and microstructure of the weld metal. Observational models on microhardness and tensile strength at the midway of weld versus flux mixture elements and BI have been formulated [33]. Kanjilal et al. noticed that in submerged arc welding (SAW), mixed behavior of flux and welding parameters on fused weld metal chemical or mechanical properties was observed by using the mathematical model approach [34]. Beidokhti et al. investigate the effect of Ti on API 5L-X70 steels to weld metal properties at manganese levels of 1.4 and 2%. Excellent mechanical behaviour in the weld series was achieved in two configurations, i.e. 1.92%Mn-0.02%Ti and 1.40%Mn-0.08%Ti. With the addition of titanium in the range of 0.02-0.08% acicular ferrite in the microstructure was expanded [35]. Deng et al. study, the role of titanium-enriched carbon-nitride on the Charpy impact and tensile behaviour of two X80 line pipe plates and their microstructures and fracture characteristics were also analyzed. The higher amount of Ti content, coarse cubic titanium-enriched inclusions, chain-type titanium-enriched precipitations, lathy bainite, a mass of martensite/austenite (M/A) inclusions were observed which results in poor toughness but high tensile strength. All kinds of these inclusions (especially chain-type Ti-enriched) present in the weld metal are sources of cracks at fracture. At very low temperature conditions negative effects of increased titanium content results in inferior impact properties [36]. Trindade et al. observed the influence of Ni content (0.50 wt. %-3.11 wt. %) on the toughness and microstructure of CMn fused metals obtained from submerged arc welding (SAW). Ni amount up to 1 wt.% enhances the weld impact value due to gain of acicular ferrite content and microstructural refinement. At higher nickel content, due to the existence of micro constituent martensite-austenite (M-A) weld metal toughness reduced [37]. North et al. studied the various parameters influencing the impact properties of CMnCb and CMn welds. Multipass welds addition of aluminium in CMn deposits was beneficial, but were negative in case of CMnCb welds. The influence of Mn, Si, Al or Mg on the impact behavior of CMn and CMnCb welds depends upon cooling rate after welding. At high cooling rate notch toughness value observed to be detrimental as compared to low cooling rate. Titanium and vanadium mixing in low oxygen CMn and CMnCb welds promote acicular ferrite microstructure, but nitride composing mixings such as zirconium and aluminium did not develop the acicular ferrite microstructure [38]. Chai et al. reveal that by producing binary CaF_2-metal oxide fluxes in submerged arc welding the stability of metal oxides was commonly studied. The oxides investigated to include MnO, MgO, SiO_2, Al_2O_3, TiO_2, K_2O, Na_2O and CaO. Bhatti et al. studied to stimulate the high dilution situation in practical pipe manufacture a range of submerged arc welds beads made on API 5LX65 base material were investigated. With the advent of technology toughness requirements for arctic grade line pipe have become increasingly more stringent. API graded steel provides excellent protection against hydrogen embrittlement in pungent gas conditions and these rare earth elements have an indirect effect on the behaviour of SAW weld by generating a micro-structural phase known as acicular ferrite. Acicular ferrite phase known to optimize toughness properties in unrefined weld metal. It was noticed the level of acicular ferrite in the weld bead is lower in Ca-treated than in Ca-free base metal for similar welding conditions and use of microalloyed welding wire promote the highest level of acicular ferrite for both calcium-treated and calcium-free base metal [39]. Palm et al. observe the influence of electrochemical and thermo-chemical interactions on the weld metal chemistry in a submerged arc welding (SAW). During chemical reactions there is a movement towards flux constituents of the pool and favor overall composition of thermal-chemical equilibrium. Manganese content higher in metal than in flux, therefore manganese decomposition from metal to flux was reported while Si amount was larger in flux, therefore thermo-chemically Si pickup by welding metal was noticed. Thermo-chemical and electrochemical distribution were greatly affected by low or high welding speeds, total current flowing per unit volume, higher temperature and reaction time before solidification [40]. Yoshino et al. studied the effect of niobium microalloy welds to improve low-temperature notch toughness and strength. It was observed that the presence of above optimum level of niobium (0.03%) in the weld metal was greatly injurious to impact behaviour because of the precipitation of niobium carbo-nitrides. To achieve high value of toughness in the weld metal various steps were taken despite niobium pick up such as, basic flux used rather than acidic, weld metal carbon content should be minimum, alloy constituents such as Ni and Mo should be mixed to overcome an upper bainite and pro-eutectoid ferrite and promote acicular ferrite [41].

2.3. Correlation of Physico-chemical behaviour with flux constituents

The physicochemical properties and chemical composition of a coating mixture depends on the raw material and have a significant effect on the penetration depth [42-43]. Alkaline and alkali oxides develop the vapours that more easily ionized and thus produce a stable arc. Vapors produced by MnO, FeO, NiO, CuO, and TiO_2 have average ionization potential and have a small influence on the stability of arc. Al_2O_3 and Cr_2O_3 have also decreased the arc stability [44]. Between metal and flux, there was an increase in reaction rate of flux having low viscosity due to the dispersal of components from the metal-slag interface was high. With low viscous flux more heat transfer takes place [45]. TABLE 4 represents the physico-chemical behaviour of fluxes.

Atoms of gas cannot enter rapidly through the flux if the viscosity of flux is higher. To dissolve and transport, these gaseous elements and flux must have a low enough viscosity [47]. Heat input and flux composition had a strong effect on arc penetra-

TABLE 4

Flux behaviors related with physico-chemical properties [46]

Physico-chemical properties	**Flux behaviour**
Arc Stability	a) Flux containing material of various ionization potentials can affect the arc stability. FeO and CaO are easily ionized atoms and due to greater oxygen potential in arc cavity give better stability of arc. b) Alkali metals quickly react with water and generate vapors which are easily ionized, and stabilize the arc.
Viscosity	a) Basic flux decreases the fluidity or increases viscosity with the increase in the amount of acidic part. On addition, of MnO and CaO in the slica network, the amount of silicon oxygen bonds is decreased. b) The viscosity of the flux should always be having smaller value because if the flux viscosity is high, the atoms of gas cannot dispense quickly over the flux and approach the metal flux pool before the flux solidification. c) If the flux viscosity increases higher up to a certain limit (above 7poise) pocking will occur in the weld metal. Pock marks are the residual oxide in the flux and share oxygen to the weld pool.
Slag detachability	a) Slag pillar in multi-pass weldments are improved by residual slag on the weld deposit. b) Deterioration resistance of the weldments is also reduced by slag detachability. c) The chemical and physical properties in the flux also correlated with slag detachability. d) When the flux containing gases and fluorite, poor slag removal is observed. Slag with [Cr,Mn,Al_2O_3, Cordierite] and [Cr, MgO, MnO] type spinel phases are difficult to remove.

tion [48-49]. Weld bead morphology is widely affected by flux viscosity which is controlled by various flux constituents. Molten weld confined to a flux having high viscosity enlarge the heat input for a disposed area and ensuring wider penetration. To yield maximum refining, protection requirements and appropriate weld bead morphology the flux viscosity must be optimized. Viscosity of basic fluxes decreases to increase in the amount of Fe_2O_3, CaO, MnO, CaF_2 and Al_2O_3. In both acid and basic fluxes the silica additions tend to boost the viscosity [50]. Above three ionic percent, Fe^{3+} ions are more competent in raising the viscosity of flux than Ca^{2+} ion additions [45]. Maintenance and initiation of arc and weld bead morphology are greatly influenced by flux constituents. For producing fixed heat input and a homogeneous weld bead the arc voltage should not greatly fluctuate [51-53]. Flux plays an important role by providing easily ionized atoms in welding for improving arc stability. With increasing Fe^{++} and Ca^{++} content arc instability of steel found to be decreased. Calcium is of smaller value of ionization potential than manganese responsible for decreasing the arc stability. Both manganese and iron have equal value of ionization potential and little change in arc stability occur [54].

3. Mechanical, Microstructural and Structural Integrity issues

3.1. Effect of flux elements on mechanical and micro-structural properties of weld metal and HAZ pipeline steel welds

For the use of pipeline welds in harsh environment the mechanical properties of fused metal and heat affected zone (HAZ) plays an important role. During submerged arc welding excessive heat is produced at the joint – metal interfaces near the HAZ. Excessive heat of welding imposes thermal cycles that lead to interfacial coarse grain regions to form local brittle zones in the heat affected region [55-56]. As to heat input at welding 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 [57-58]. Presence of hard martensite/austenite phase in the microstructure deteriorates the impact toughness and also the crack tip open distance value decreases with the increase in volume fraction of martensite/austenite [59-60]. There are several methods addressed to enhance the impact behavior of HAZ. TABLE 5 shows the various methods of improving HAZ toughness of pipeline steel.

TABLE 5

Method of improving HAZ toughness of pipeline

I. Modification of matrix alloy	Contribution of Ni
II. Reduction in martensite/	Decrease in carbon equivalent and carbon content valueaustenite constituents
III. Refinement of grain size	Large HAZ impact behaviour with fine microstructure provided by (HTUFF) procedure.
	Formation of intergranular ferrite and Suppression of austenite grain coarsening near fusion line.
	Titanium-oxide method
	From nucleated precipitate such as Ti oxide, utilization of intergranualer ferrite.
	TiN method
	Fine particles such a suppression of austenite grains.

Notch Toughness for CMnCb deposits containing aluminium and titanium also observed. Deposit oxygen content remarkably decreased up to 100 ppm with the addition of titanium and toughness properties also improved, but notch toughness greatly impaired by the addition of aluminum [61]. Vanadium and titanium develop acicular ferrite structure in CMnCb deposits but Zr and Al (aluminum) don't. TABLE 6 represents the effect of different micro alloying consituents on the microstructure CMnCb deposits.

TABLE 6

Effect of Ti, Al, Mn, Zr and V on microstructure CMnCb deposits

Flux element	**Flux type**	**Flux element amount**	**O_2 content**	**Microstructure**
Mn	CMnCb	increased	increased	Do not formed Acicular ferrite
Ti	CMnCb	increased	Lower	Acicular ferrite + Pro-eutectoid ferrite
Al	CMnCb	increased	increased	Bainitic structure
Zr	CMnCb	Increased (upto 1.4 %)	Lower	Do not formed Acicular ferrite
V	CMnCb	increasd	<200 ppm	Acicular ferrite

Vanadium and titanium exhibit acicular ferrite in low oxygen content deposit due to variation of inclusion content dispersal previous to austenite grain size or intragranular nucleation of ferrite laths. Within the grains of acicular ferrite the oxide formation exhibits the role of nuclei [62-65]. Acicular ferrite content was markedly decreased when Zr was mixed with titanium and V-bearing deposits because zirconium has a large attraction for nitrogen than vanadium or titanium. Acicular ferrite microstructure has been affected by zirconium addition by interfering with TiN and VN formation [62]. Both TiN and ZrN virtually insoluble in austenite and formed as carbide particles in steel melt [66-67]. Because of fine size and resistance to crack propagation the acicular ferrite provided with good tensile strength and toughness to the welds, so it is better to expand the total portion of ferrite in the joints [68]. There are several methods that favor the formation of acicular ferrite includes various oxides such as vanadium oxide, titanium and boron oxide. Dissolution of various metallic components and oxygen in the weld interface takes place when oxides in the flux contributed [69]. When metallic elements reacted, the oxide inclusions are formed which enclosed into the weld and promote the nucleation of acicular ferrite structure during the cooling of weld [70-71]. Equivalent carbon content related to the hardness and tensile strength of steel [71]. Mo, V, Si, Mn, Ni and C represent the percentage of metallic contents. The weld metal with greater and small carbon equivalent higher and lower hardness and tensile strength obtained. A high sensitivity to cold cracking after welding obtained when corresponding carbon content greater than 0.45 and also during cooling of welds the martensite structure formed [72]. Equation 1 shows the formula used to calculate the equivalent carbon content in low alloy steels.

$$CE_{IIW} = C + Mn/6 + Cr/5 + Mo/5 + \\ + V/5 + Ni/15 + Cu/15 \qquad (1)\ [72]$$

Notch toughness greatly reduced with the addition of niobium (above 0.03%) in the weld metal it happens because during the transformation of weld metal after deposition, there is precipitation of niobium carbo-nitrides takes place. Up to 65% of Nb pick up in the weld produced during submerged arc welding even with Nb-free filler materials. The volume of pro-eutectoid ferrite reduced and that of acicular ferrite enlarged with the incorporation of niobium, but the issue was composed only by 0.03% Nb. In submerged arc welding notch toughness greatly affected by the interaction of niobium with other alloying elements [73]. The effect of Nb on pro-eutectoid ferrite reduced with the addition of 0.3% Mo. Mo decrease the dislocation density of Nb-bearing weld metal. Acidic fluxes produce higher oxygen as compared to basic flux. Transition temperature broadly affected with the addition of the basic flux to the acidic flux and simultaneously the notch toughness of the seam welds also modified [74]. Strength and toughness properties are functions of carbon (C), niobium (Nb) and vanadium (V). At low carbon (0.08%) with the addition of niobium and at high carbon (0.18%) addition of vanadium the heat affected zone toughness increased, but together with the addition of vanadium and niobium decreased the heat affected zone toughness [75]. TABLE 7 respresents the effect of micro-alloying components on various mechanical properties of pipeline welds.

3.2. Effect of Diffusible Hydrogen content on submerged arc welding fluxes

Among all basic oxides, it is calcium oxide that has larger ability to absorb and fix water in the structure and having excellent capability of reducing hydrogen and oxygen contents in the molten arc. Higher the carbonate fraction, the higher the basicity of slag and lower the hydrogen content in a weld. The suitable fluidity of molten slag and the reduction in diffusive

TABLE 7

Impact of micro-alloying components on hardness, microstructure and notch toughness of pipe weld

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			

hydrogen content were obtained by adding constituents containing fluoride ions [76]. Hydrogen embrittlement is generally more susceptible to high strength weld metals due to metallurgical changes required to strengthen them. One reason is that in previous study fracture may generate and start with lower hydrogen levels without relying on the transfer of that component by disruption on 45-degree slip bands. The second reason may be the proportionate depression of the grain boundaries as the matrix is strengthened, offering simple, preferred direction for crack growth. Chevron cracking was observed at the high hydrogen level and electron fractography demonstrated that both the transcolumnar and intercolumnar crack components were formed at small temperature. Tuliani studied the performance of laboratory and industrial cracks using various modern microscopy techniques [77]. TABLE 8 represents the different cracks observed in submerged arc weldments.

To identify the major factors which control the final oxygen level in the weld metal it was desirable to access and evaluate various kinds of reactions taking place during welding. It was reported wire, fluxes and parent plate of known compositions the corresponding variations take place from one step to another during slag-metal operations. The metal droplet stage and electrode tip are the major sites for oxygen absorption. At weld metal stage, serious depletion of oxygen, as well as metallic species such as Al, indicated the separation of oxidation products are the most significant factor determining final oxygen content. The metallurgical behaviour of coating mixture and significant toughness of the weld is expressed by equation (2). Basicity is commonly used to describe the metallurgical behavior of a welding flux. The basicity index is a ratio between basic and acid compounds (oxides and fluorides) of which the flux is composed. Basicity has great influence on impact toughness of the weld metal. Increasing basicity brings down the oxygen content and hence the inclusion level in the weld metal. Consequently, the impact toughness will increase. Lower the hydrogen content and greater the toughness of weld [78-80].

$$\begin{aligned}\text{Basicity Idex (BI)} = (&\mathrm{MgO} + \mathrm{CaO} + \mathrm{SrO} + \mathrm{BaO} + \\ &+ \mathrm{K_2O} + \mathrm{Na_2O} + \mathrm{Li_2O} + \mathrm{CaF_2} + \\ &+ 0.5\,(\mathrm{FeO} + \mathrm{MnO}))/(\mathrm{SiO_2} + 0.5(\mathrm{FeO} + \mathrm{MnO}))\end{aligned} \tag{2}$$

3.3. Effect of Cooling behaviour and chemical content

Cooling rate and weld metal composition (alloying elements and oxygen content) are the prime parameters that predicts the microstructural behaviour in weld region. It is reported that growing cooling rate tends to change the microstructure from grain boundary ferrite to side plate ferrite, acicular ferrite, bainite and eventually to martensite [81]. Yan et al. observed that rapid cooling succeeded by large heat input SAW welding process decreases the size of HAZ and coarse-grained region in the naval steel. The optimum decrease in austenite grain size (from 40 to 25 μm) and essentially smaller content of remaining MA (5.36 in case of rapid cooling and 11.6 in case of traditional cooled ones) lead to a tremendous enhancement in the low temperature impact behavior of testing specimens [82]. Toughness is greatly influenced by cooling rate. Grain coarsening and precipitation takes place when cooling rates are relatively slow. Grain refinement takes place when Cb and V added to the steel at fast cooling and thus the toughness of heat affected zone increased by suppressing the proeutectiod steel [83]. Weld metal properties are widely affected by the chemical composition [84]. Filler metal composition, parent metal dilution, type of flux and metallurgical, chemical interactions in the weld pool alter the composition of weld metal [84-86]. For large diameter pipelines, there are several factors responsible for the selection of chemical composition of wire for submerged arc welding (SAW) of high strength low alloy steel such as formation of acicular ferrite microstructure for weld metal, the addition of micro-alloying elements to raise the impact behaviour and strength value of weld metal, the wire is cleaned to reduce the amount of sulfur, phosphorus, hydrogen, oxygen and nitrogen and low carbon content is utilized [87]. Two major accesses to enhance the impact behaviour of fused metal; one is to change of filler metals and is use of different fluxes [88-89]. The development of acicular ferrite in the microstructure with the addition of titanium and boron results in better mechanical properties. Not only suitable combination of alloying elements and cooling rate, but appropriate inclusions distribution, promote the formation of acicular ferrite in the microstructure [90-91]. Increasing the content of acicular ferrite the DBT reduced and the dispersion of fine oxide inclusions takes place with the addition of titanium, which facilitates development of acicular ferrite in the microstructure [92]. Presence of fine interlocking laths of acicular ferrite and martensite/extent as a second phase in the microstructure shows the highest resistance to cleavage fracture because the microstructure containing pro-eutectoid ferrite promote the cracks propagation easily [92-93]. Better mechanical properties and acicular ferrite microstructure observed in weld metal when titanium and manganese combined with suitable composition such as 1.92%Mn-0.02%Ti (high Mn and low Ti) and 1.40%Mn-0.08%Ti (low Mn and high Ti) The recovery of Mn raised and the nucleation of acicular ferrite reduced with the addition of titanium beyond optimum level (0.02-0.05%).

TABLE 8

Cracks formation observed during submerged arc welds at high temperature [19]

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

Weld microstructure homogenize and refines with the addition of manganese while more addition of titanium (above 0.08%) and manganese (above 2%) results increased hardenability due to more grain boundary nucleation of bainite as compared to the intergranular nucleation of acicular ferrite [89]. Molybdenum is not suitable for toughness or having deleterious for toughness when added with 1% manganese but together with 1.5% manganese and 0.25% molybdenum provide maximum toughness value [94]. Segregation of manganese and phosphorous affected by the increase in manganese content which produces sensitivity to temper embrittlement and leads to phosphorous enrichment at the grain boundaries [95]. For solid solution strengthening the manganese is an important alloying constituent and in steels, the centerline micro- structural banding decreases as manganese content reduced [96]. Segregation of grain boundaries and reduction in the boundary energy take place with the addition of B (boron) in the fused metal, as a result, uniform nucleation is restricted and the extent of ferrite and bainite decreased thus acicular ferrite formed at inclusions. Boron easily forms compounds with oxygen and nitrogen and generally, Ti is mixed to the weld wire to shield the boron. Titanium entraps carbon and nitrogen and makes boron available for grain boundary segregation due to this reason B-Mo-Ti wires developed for submerged arc welding process [97-98]. Addition of chromium in weld metal promotes the development of acicular ferrite, but reduces the impact toughness value and also rise in the carbon amount reduces impact behaviour and increase brittleness as a result of the formation of the second phase in the microstructure i.e. martensite/austenite phase [99]. At relatively lower silicon content, i.e., 0.03-0.26 wt-% acicular ferrite formed in the microstructure and improves the toughness value slightly while at higher silicon content varies 0.42 to 0.95 wt-% the acicular ferrite in the microstructure was not formed [100]. TABLE 9 represents the effect of various micro-alloying constituents on the mechanical as well as microstructural behaviour of welds.

3.4. Role of slag in controlling physico-chemical and mechanical properties

Slag properties have a decisive effect on both qualities of the product and process control. To improve the product quality the physicochemical properties of slags need to solve. To estimate the thermophysical behaviour of slags a significant number of mathematical models have been reported. For viscosity measurement a large number of models are available but for thermal or electrical conductivity measurement only a few models are reported [101-102]. The mechanical properties of steel are dependent on the absorption of inclusions in the flux because both numeral and the proportion of inclusions affect its properties. Consumption of inclusions involves several steps (1) passage of inclusions to the slag/metal interface, (2) disintegration of the inclusions in slag bed, (3) attainment of essential surface tension properties [103-105]. The disintegration of inclusion from steel to flux is encouraged by the large contact angle between inclusion and metal respectively. The high value of (C_{Sat}-C) is promoted by dissolution of inclusions in the flux. If more inclusion remains undissolved in the slag bed result in an increase the viscosity and affect other properties drastically [106]. TABLE 10 shows the influence of various flux elements on different slag properties.

3.5. Effect of structure and different cations on the thermo-physical properties of slag

Various slag properties like surface tension, electrical conductivity, thermal conductivity, viscosity density, enthalpy and heat capacity depend upon the structure of slag. Viscosity, density thermal and electrical conductivity are the most competent properties which have a strong effect on the structure of slag while the change in enthalpy and heat capacity has not much influ-

TABLE 9

Effect of Ti, Mn, Mo, Cr and C on the mechanical behaviour and microstructure of weld metal [95-98]

Flux element (Wt-%)	**Mechanical properties**	**Microstructure**
	Hardness toughness YS UTS	**AF B WF GBF M/A**
Ti (>0.08%)	Increase Decrease Increase Increase	NF F … … F
Ti (0.02-0.05%)	Decrease Increase Decrease Decrease	F NF NF NF NF
(1.92%Mn-0.02%Ti)	Decrease Increase Decrease Decrease (best impact toughness value)	F NF NF NF NF
(1.4%Mn-0.08%Ti)	Decrease Increase Decrease Decrease	F NF NF NF NF
Ti + Mn (up to optimum level)	Decrease Increase Decrease Decrease	F NF NF NF NF
Ti + Mn (above optimum level	Increase Decrease Increase Increase	F F F F F
(0.25%Mo + 1.5%Mn)	… increase …. ….	F NF … … F
Cr	… decrease …. ….	F N F … … NF
C	Increase Decrease Increase Increase	NF N F … … F
Ni (2.03-2.91%) +Mo(0.7-0.999%)	Decrease Increase Decrease Decrease	F N F … … NF
Ni (2.03-3.75%)	---- Greatly decrease ---- ------	NF F --- -- F
Si (0.03-0.26%)	---- Slightly decrease ---- ------	F ….. …. …. ……
Si (0.42-0.95%)	… decrease …. ….	NF F --- -- F

Notations: AF-Acicular ferrite; B-Bainite; WF-Widmenstanten ferrite; GBF-Grain boundary ferrite; M/A-Martensite-asutenite; YS-Yield strength; UTS--Ultimate tensile strength; F-Formed; NF-Not Formed

TABLE 10

Influence of various flux constituents on the mould flux behaviour [106]

Property	CaO	SiO_2	Al_2O_3	$Na_2O + K_2O$	MgO	FeO	CaF_2	MnO	B_2O_3	ZrO_2
V	↓	↑	↑	↓	↓	↓	↓	↓	↓	—
BT. (T_{br})	↑	↓	↓	↓	↓	↓	↓	↓	↓	↑
ST	↑	↓	↓	↓	↑	↓	↓	↓	↓	↑
IT	↑	↓	↑			↓		↓		
T(k)	↓	↑	↑		↓					
CT	↑	↓	↓	↓	↓		↑	↓	↓	↑

Note: V: viscosity; BT: break temp.; ST: solidification temp.; IT: interfacial tension; T: thermal cond.; CT: crystallinity

ence on the structure [107-108]. The interaction between slags is commonly electrochemical in nature and generally requires the interchange of ions. Each of negatively charged oxygen ions (O ions) can associate with one of two O^- ions and act as network known as bridging oxygen (O°), while those ions which break the chain are known as network breaker and act as non-bridging oxygen (NBO or O^-). Those ions which do not take part in network association with silicon ions are known as free oxygen denoted by O^{2-}. By finding the mole fractions of BO, NBO or FO (free oxygen) the structure of slags can be represented and for this, it is necessary to distinguish the constituents which are network former (e.g. SiO_2) or network breakers (CaO, Na_2O etc.) [109-111]. Al^{3+} ion can be absorbed the Si^{4+} chain, when Al_2O_3 is added to silicate slag.

3.6. Parameters used to represent structure

To represent the structure of slags various parameters have been used. In earlier models basicity and basicity indices were used to assign different load to various oxides such as CaO, MgO or FeO. The frequently applied factor is NBO/T (number of non-bridging oxygen/ tetragonally-bonded oxygen), Q and Λ which are calculated by equation (1), (2) and (3). Optical basicity is widely used to represent the structure [112-117].

Where

NBO/T – represents the de-polymerisation of slag
Q – represents the polymerisation of slag
Λ – used to measure structure of slag

$$\mathrm{NBO/T} = 2(X_{FeO} + X_{Na2O} + X_{CaO} + X_{MnO} + 2X_{TiO2} + X_{MgO} + \\ + X_{K2O} + 3fX_{Fe2O3}/X_{SiO2} + 2X_{Al2O3} + 2X_{Fe2O3} \quad (1)$$

where X – mole fraction

$$Q = 4 - (\mathrm{NBO/T}) \quad (2)$$

$$\Lambda = \sum(X_1n_1\,\Lambda_1 + X_2n_2\,\Lambda_2 + X_3n_3\,\Lambda_3 + X_4n_4\,\Lambda_4 + \ldots\ldots..) / \\ \sum(X_1n_1 + X_2n_2 + X_3n_3 + \ldots\ldots.) \quad (3)$$

Where n – oxygen present in oxide.

Λ_1, Λ_2 etc are the recommended optical basicity values for different slag constituents [116-117].

4. Conclusions and future direction

Major key challenges that have been encountered by many researchers while joining of pipeline steels have been discussed below:

- Due to increased demand for oil and gas industry, the demand in transmission of oil and gas also increased. With the change in the manufacturing process, development of higher strength pipe line steel also increased in the market (X42, X52, X60, X65, X70, X80 and X100 respectively). With a change in the grade of line pipe steel the susceptibility of cracking also increased because as the carbon content increased the cracking tendency also increased as X80 is more susceptible to cracking as compared to X70.
- Fabrication method of joining of line pipe steel also changed from manual metal arc welding (MMAW) to automatic welding processes like pulsed GMA welding, SAW etc. Automatic techniques generate more heat input which is concentrated totally on the joint as compared to conventional welding processes.
- Weldability of line pipe steel controlled by the appropriate selection of flux chemical composition which is a complex task. Slag detachability, arc stability, viscosity, density, thermal and electrical conductivity, thermal expansion coefficient depends upon the flux composition. Physico-chemical properties of fluxes decide the mechanical behaviour of the particular line-up joint. Poor notch properties were observed with acidic fluxes as compared to basic fluxes because, in acidic fluxes, there is a chance of oxide inclusion due to the presence of acidic oxides such as SiO_2. Dissolution of inclusions is very important to achieve better mechanical properties because undissolved inclusion will remain in the slag/metal interface and creates defects in the final weld. Controlling physical, chemical and thermal properties of flux/slag the mechanical properties of line pipes can be improved.
- Microstructure affects the mechanical behaviour of pipeline steel. Development of different phase in the fluxes helps us to classify the various oxides formed and enables to know what type of anions and cations may exist in the electric arc. As the grades of line pipe steel increases (X70-X100) the microstructure changed to bainitic transformation with more yield strength as compared to previous lineup grades.

- The microstructure of line pipe steel widely affected by the cooling rate as well as weld metal composition. It is reported that increase in the cooling effect refines the microstructure from GBF to SPF, AF, bainite and eventually to martensite. In submerged arc welding, rapid cooling followed by maximum heat input decreases the size of HAZ for pipeline steel. Notch Toughness also greatly influenced by cooling rate. Grain coarsening and precipitation takes place when cooling rates are relatively slow. Grain refinement takes place when Cb and V added to the steel at fast cooling and thus the toughness of heat affected zone increased by suppressing the pro-eutectiod steel.
- The addition of micro-alloying elements also improves the mechanical and microstructural properties of line pipe steel. Addition of titanium and boron results in better mechanical properties due to the development of AF microstructure.
- Excellent mechanical properties and acicular ferrite microstructure observed in weld metal when titanium and manganese combined with a suitable composition such as 1.92%Mn-0.02%Ti (high Mn and low Ti) and 1.40%Mn-0.08%Ti (low Mn and high Ti). Molybdenum is a strong strengthening carbide former, but lonely not suitable for improving toughness or having deleterious for toughness, when added with 1% manganese but together with 1.5% manganese and 0.25% molybdenum provide maximum toughness value.
- NBO/T, Q and Λ affects the structure of slag and principally represents the structure. Viscosity and electrical conductivity are well represented by the structure of slags because these properties are widely dependent on the structure.

It is noticed that maximum studies are reported for presently used pipeline grades- X60, X65 and X70. The effect of various physicochemical properties of submerged arc fluxes needs to be elaborated to solve different structural integrity issues (such as corrosion and hydrogen embrittlement etc.) which have a serious effect on the performance of the line pipe steel. To resolve the different fabrication and structural integrity issue, it is important to study the effect of various physicochemical properties of submerged arc welding (SAW) fluxes on newly available line pipe grade (X70 to X80).

REFERENCES

[1] J.M. Grey, An independent view of linepipe and linepipe steel for high strength pipelines, Microalloying International, LP, Houston, Texas, X80 pipeline cost workshop **1**, 20 (2002).

[2] P. John, X80 Line pipe for small diameter (DN450 and smaller) high strength pipelines. Confernece preprints, Australian Pipeline Industry Association Research and Standards Committee **2**, 30 (2002).

[3] Tasak, Edmund, Ziewiec, Aneta, Spawalnosc materialow konstrukcyjnych. In: Spawalnosc stali. Wydawnictwo JAK. Krakow. **1**, 11 (2009).

[4] P. John, X80 linepipe for large diameter high strength pipelines, Confernece preprints, Australian Pipeline Industry Association Research and Standards Committee **2**, 12 (2002).

[5] S.R. Nathan, V. Balasubramanian, S. Malarvizhi, A.G. Rao, Effect of welding processes on mechanical and microstructural characteristics of high strength low alloy naval grade steel joints, Defence Technology **11**, 308-317 (2015).

[6] K. Akao, T. Ishihara, T. Kitada, Y. Nishino, N. Okuda, Improvement of Notch Toughness and Soundness in Longitudinal Seam weld of Line pipe, Trans. ISIJ **26**, 379-385 (1985).

[7] J. Palm, Shielded Metal Arc Welding Consumables for Advanced High Strength Steels, Work performed under Contract N00014-89-J-3170, annual Progress Report.

[8] P.D. Hodgson, S.H. Zahiri, J.J. Whale, ISIJ Int. **44**, 1224 (2004).

[9] D.S. Ivani, Bott, F.G. Luis, S. De, C.G. Jose, Metallurgical and Materials Transactions A **36**, 443, (2005).

[10] H. Tamehiro, H. Asahi, T. Hara, Y. Terada, United States Patent 6264760 1, (1999).

[11] V. Philip, Specification for line pipe, ISO 3183:2007 (modified), petroleum and natural gas industries-steel pipe for pipeline transportation system, ANSI/API specification 5L, forty-fourth edition 1, (2007).

[12] P. Venton, Design Constraints against the use of X80 for Australian Pipelines, Australian Pipeline Industry Association Research and Standards Committee **1**, (2002).

[13] P. Bilston, M. Sarapa, International use of X80 Pipelines, GHD Pty Ltd Australia, Australian Pipeline Industry Association Research and Standards Committee **2**, (2002).

[14] H.G. Hillenbrand, C.J. Heckmann, K.A. Niederhoff, X80 line pipe for large-diameter high strength pipelines, Germany Mannesmann Forschungsinstitut **1**, (2002).

[15] H. Engelmann, A. Engel, P.A. Peters, First use of large-diameter pipes of the steel GRS 550 TM (X80); 3R International **25**, 182-193, (1986).

[16] V. Chaudhari, H.R. Ritzmann, G. Wellnitz, German gas pipeline first to use new generation line pipe,Oil & Gas Journal **1**, (1995).

[17] H.G. Hillenbrand, K.A. Niederhoff, G. Hauck, E. Perteneder, G. Wellnitz, Procedure considerations for welding X80 line pipe established, Oil & Gas Journal 1, (1997).

[18] C.S. Chai, T.W. Eagar, The effect of SAW parameters on weld metal chemistry. Weld J. **59**, 93s-98s (1980).

[19] S.H. Hashemi, D. Mohammadyani, Characterisation of weldment hardness, impact energy and microstructure in API X65 steel, International Journal of Pressure Vessels and Piping **98**, 8-15, (2012).

[20] F. Singer, S. Singer, Enciclopedia de la Química Industrial Tomo, Cerámica Industrial **9**, 84-314, (1979).

[21] M.L.E. Davis, N. Bailey, Evidence of Inclusion Chemistry for Element Transfer Submerged Arc Welding, Welding Research Supp. **70**, 5 (1991).

[22] B. Beidokhti, R. Pouriamanesh, Effect of Filler Metal on Mechanical Properties of HSLA Welds, Welding Journal **94**, 334-341 (2015).

[23] R.D.Thomas, Submerged-Arc Welding of HSLA Steels, Metal Progress **111**, 30-36 (1977).

[24] J.T. McGrath, R.S. Chandel, R.F.Orr, J.A.Gianetto, A Review of Factors Affecting the Structural Integrity of Weldments in Heavy Wall Reactor Vessels, Canadian Metallurgical Quarterly **28**, 75-83 (1989).

[25] J.H. Palm, How fluxes determine the metallurgical properties of submerged arc welds **2**, 358-360 (1972).

[26] C.S. Chai, T.W. Eagar, Slag metal reactions in binary CaF_2-metal oxide welding fluxes, Welding Research Supp. **1**, 229-232 (1982).

[27] K. Bang, C. Park, H.C. Jung, J.B. Lee, Effects of Flux Composition on the Element Transfer and Mechanical Properties of Weld Metal in Submerged Arc Welding, Met. Mater. Int. **15**, 471-477 (2009).

[28] Y. Peng, W. Chen, Z. Xu, Study of high toughness ferrite wire for submerged arc welding of pipeline steel, Mat. Charact. **47**, 67-73 (2001).

[29] S. Jindal, R. Chhibber, N.P. Mehta, P. Kumar, Design and Development of Fluxes for Submerged Arc Welding of HSLA Steel, International Journal of Surface Engineering & Materials Technology **3**, 2249-7250 (2013).

[30] D. Bhandari, R. Chhibber, N. Arora, R. Mehta, Investigation of TiO_2-SiO_2 –CaO-CaF_2 based electrode coatings on weld metal chemistry and mechanical behavior of bimetallic welds, Journal of Manuf. Proc. **23**, 61-74 (2016).

[31] S. Brijpal, K.A. Zahid, S.N. Arshad, M. Sachin, Effect of CaF2, FeMn and NiO additions on impact strength and hardness in submerged arc welding using developed agglomerated fluxes, Journal of Alloys and Compounds **1**, 20-30 (2016).

[32] K. Ajay, H. M. Singh, M. Sachin, Modelling and Analysis by response surface methodology of hardness for submerged arc welded joints using developed agglomerated fluxes, Indian Journal of Engineering & Material Science **19**, 379-385 (2012).

[33] S. Jindal, R. Chhibber, N. P. Mehta, Effect of flux constituents and basicity index on mechanical properties and microstructural evolution of submerged arc welded high strength low alloy steel, Mat. Sci. Forum **738**, 242-246 (2013).

[34] P. Kanjilal, T.K. Pal, S.K. Majumdar, Combined effect of flux and welding parameters on chemical composition and mechanical properties of submerged arc weld metal, Journal of Mat. Proc. Techn. **171**, 223-231 (2006).

[35] B. Beidokhti, A.H. Koukabi, A. Dolati, Influences of titanium and manganese on high strength low alloy SAW weld metal properties, Mat. Charact. **6**, 225-233 (2009).

[36] D. Wei, G. Xiuhua, Z. Dewen, D. Linxiu, W. Di, W. Guodong, Effect of Ti-enriched Carbonitride on Microstructure and Mechanical Properties of X80 Pipeline Steel, Journal of Mater. Sci. Technol. **26**, 803-809 (2010).

[37] B.V. Trindade, C.D. Payao, J. Souza, G.F.L. Paranhos, The role of addition of Ni on the microstructure and the mechanical behaviour of C-Mn weld metals, Exacta **5**, 177-183, (2007).

[38] T.H. North, H.B. Bell, A. Koukabi, I. Craig, Notch Toughness of Low Oxygen Content Submerged Arc Deposits, Welding Journal Supp. **1**, 343-354 (1979).

[39] A.R. Bhatti, M.E. Saggese, D.N. Hawkins, J.A. Whiteman, M.S. Golding, Analysis of Inclusions in Submerged Arc Welds in Micro alloyed Steels, Welding Research Supp. **1**, 224-230 (1984).

[40] J.H. Kim, R.H. Frost, D.L. Olson, M. Blander, Effect of Electrochemical Reactions on Submerged Arc Weld Metal Compositions, Welding Research Supp. **1**, 446-454 (1990).

[41] Y. Yoshino, R.D. Stout, Effect of Microalloys on the Notch Toughness of Line Pipe Seam Welds, Welding Research Supp. **2**, 59-68 (1979).

[42] B. Singh, Z.A. Khan, A.N. Siddiquee, Review on effect of flux composition on its behavior and bead geometry in submerged arc welding, Journal of Mech. Engg. Res. **5**, 123-127 (2013).

[43] D.D. Schwemer, D.L. Olson, D.L. Williamson, Relationship of weld penetration to the welding flux, Welding Research Supp. **2**, 153-160 (1979).

[44] J.D. Plessis, M.D. Toi, P.C. Pistorius, Control of diffusible weld metal hydrogen through flux chemistry modification, Weld J. **86**, 273s-280 (2007).

[45] N.D. Pandey, A. Bharti, S.R. Gupta, Effect of submerged arc welding parameters and fluxes on element transfer behaviour and weld-metal chemistry, J. Mater. Process. Tech. **40**, 195-211 (1994).

[46] P. Kanjilal, S.K. Majumdar, T.K. Pal, Prediction of acicular ferrite from flux ingredients in submerged arc weld metal of C-Mn steel, ISIJ Int. **45**, 876-885 (2005).

[47] U. Mitra, T.W. Eagar, Slag metal reactions during submerged arc welding of alloy steels, Metall. Trans. A. **15**, 217-227 (1984).

[48] J.L. Wilson, G.E. Claussen, C.E. Jackson, The Effect of I^2R Heating of Electrode Melting Rate, Welding Journal **35**, 1-8 (1980).

[49] C.E. Jackson, A.E. Shrubsall, 1953, Control of Penetration and Melting Ratio with Welding Techniques, Welding J. **32**, 172-178 (1953).

[50] H.E. Janzen, An Investigation of the SiO,-MnO-CaO/CaF2 Welding Flux System, Thesis, Colorado School of Mines **1**, 1-7 (1977).

[51] M. Bertung, Influence on DC Generators and Welding Transformers on Arc Stability and Electrode Burn-Off Rate, British Welding Journal **847**, (1964).

[52] C.E. Jackson, The Science of Arc Welding-Part I, Welding lournal, Research Suppl. **39**, 129-140 (1960).

[53] B.M. Patchett, Some Influences of Slag Composition on Heat Transfer and Arc Stability, Welding Journal **53**, 203-210 (1974).

[54] C.A. Butler, C.E. Jackson, Submerged- Arc Welding Characteristics of the CaO-TiO,-SiO, System, Welding Journal **46**, 448-456 (1967).

[55] Hrivnak, Weldability of modern steel materials, ISIJ Int. **35**, 1148-1156 (1955).

[56] S. Bott, G.D Souza, J.C.G, Teixeira, P.R. Rios, Highstrength steel development for pipelines: a Brazilian perspective, Metall. Mater. Trans. A **36A**, 443-454 (2005).

[57] Y. Terada et al., High-strength linepipes with excellent HAZ toughness, Nippon Steel Tech. Rep. **90**, 88-93 (2004).

[58] C. Liu, Z.B. Zhao, D.O. Northwood, Mechanical properties of the heat-affected zone in a bainitic high strength low alloy steel, Mater. Sci. Technol. **18**, 1325-1328 (2002).

[59] S. Aihara, K. Okamoto, Influence of local brittle zones on HAZ toughness of TMCP steels, Proc. AWS Int. Conf. on 'Metallurgy, welding and qualification of microalloyed (HSLA) steel weldments', Houston, TX, USA, AWS **402**, 125-131 (1990).

[60] C. Liu, S.D. Bhole, Challenges and developments in pipeline weldability and mechanical properties, Sci. and Tech. of Weld. and Joining **2**, 181 (2013).

[61] T.H. North, H.B. Bell, A. Koukabi, I. Craig, Notch toughness of low Oxygen content Submerged arc deposit., Weld. Supp. J. **1**, (1979).

[62] Y. Ito, M. Nakanishi, Study on Charpy Impact Properties of Weld Metal in Submerged Arc Welding, IIW Doc. XIIA **75**, 1-50 (1975).

[63] A. Shiga, P.L. Imura, J. Tsuboi, Effects on Niobium and Vanadium on Toughness of Submerged Arc Weld Metal, IIW Doc. IX-1049-77, **2**, 1-21 (1977).

[64] C.L. Choi, D.C. Hill, A Study of Microstructural Progression in As-Deposited Weld Metal, Welding Journal **57**, 232-236 (1978).

[65] D.J. Abson, R.E. Dolby, P.A. M. Hart, Role of Nonmetallic Inclusions in Ferrite Nucleation carbon Steel Weld Metals, International Conference on Trends in Steels and Consumables for Welding, London **25**, 75-89 (1978).

[66] A. McLean, D.A.R. Kay, Control of Inclusions in High-Strength Low-Alloy Steels, Microalloying **75**, 215-231 (1975).

[67] T. Gladman, D. Dulieu, I. Mclvor, Structure-Property Relationships in High-Strength Microalloyed Steels, Microalloying **76**, 32-54 (1975).

[68] S. Liu, D.L. Olson, The role of inclusions in controlling HSLA steel weld microstructures, Weld. J. Suppl. Res. **65**, 139-141 (1986).

[69] G.M Evans, Microstructure and properties of ferritic steel welds containing Ti and B, Weld. J. Supplement Res. **75**, 251-254 (1996).

[70] J.M. Dowling, J.M. Corbett, H.W. Kerr, Inclusion phases and the nucleation of acicular ferrite in submerged-arc welds in high-strength low alloy steels, Metall. Trans. A. **17**, 1613-1618 (1986).

[71] C.V Eijk, O. Grong, J. Hjelen, Quantification of inclusionss-timulated ferrite nucleation in wrought steel using the SEMEBSD technique, Proceedings of the International Conference on Solid-Solid Phase Transformations'99 (JIMIC-3), Kyoto, Japan 2, 1999.

[72] J.E. Ramirez, Characterization of high-strength steel weld metals: chemical composition, microstructure, and non-metallic inclusions. Weld J. **87**, 65-75 (2008).

[73] N. Cordea, Niobium-and Vanadium- Containing Steels for Pressure Vessel Service, Welding Research Council Bulletin **203**, 1-5 (1975).

[74] Y. Yoshino, R.D. Stot, Effect of Microalloys on the Notch Toughness of Line Pipe Seam welds, Welding Res. Supp. **1**, 2-5 (1979).

[75] E.G. Signes, J.C. Baker, Effect of Columbium and Vanadium on the Weldability of HSLA Steels, Welding Research Council 2, 1-8 (1979).

[76] H. Terashima, J. Tsuboi, 1976. Hydrogen in submerged arc weld metal produced with agglomerated flux, Welding Journal of Japan **45**, 28-33 (1976).

[77] D.J. Allen, B. Chew, P. Harris, The Formation of Chevron Cracks in Submerged Arc Weld Metal, Welding Res. Supp. **2**, 212-221 (1992).

[78] T. Lau, G.C. Weatherly, A. Lean, Gas/Metal/Slag reactions in submerged arc welding using CaO-Al$_2$O$_3$ based fluxes, Welding Res. Supp. **1**, 31-38 (1986).

[79] K. Bang, C. Park, H. Jung, J. Lee, Effects of flux composition on the element transfer and mechanical properties of weld metal in submerged arc welding, Metals and Mat. Int. **15**, 471-477 (2009).

[80] I. Datta, M. Parekh, Filler metal flux basicity determination using optical basicity index, Welding Res. Supp. **2**, 68-76 (1989).

[81] C.B. Dallam, S. Liu, D.L. Olson, Flux Composition Dependence of Microstructure and Toughness of Submerged Arc HSLA Weldments, Weld. Res. Supp. **1**, 140-152 (1985).

[82] H.Q. Yan, K.M. Wu, H.H. Wang, L. Li, Y.Q. Yin, N.C. Wu, Effect of fast cooling on microstructure and toughness of heat affected zone in high strength offshore steel, Science and Technology of Welding and Joining **19**, 355-360 (2014).

[83] H. Peter et al., Weldability of Microalloyed Steels, Microalloying 75 Proceedings, Union Carbide **2**, 540-551 (1977).

[84] A. Gharavol, M.H.H. Sabzevar, A. Haerian, Influence of copper content on the microstructure and mechanical properties of multipass MMA low alloy steel weld metal deposits, 2009, Materials & Design **30**, 1902-1912 (2009).

[85] M. Zhoa, K. Yang, Strengthening and improvement of sulfide stress cracking resistance in acicular ferrite pipeline steels by nano-sized carbonitrides, Scripta Materialia **52**, 881-886 (2005).

[86]. B. Filho, W.W. Carvalho, M. Strangwood, Influence of alloying elements on the microstructure and inclusion formation in HSLA multipass welds, Mat. Charact. **58**, 29-39 (2007).

[87] Y. Peng, W. Chen, Z. Xu, Study of high toughness ferrite wire for submerged arc welding of pipeline steel, Mater. Charact. **47**, 67-76 (2001).

[88] S.D. Bhole, J.B. Nemade, L. Collins, C. Liu, Influence of nickel and molybdenum additions on weld metal toughness in submerged arc welded HSLA line-pipe steel. Journal of Materials Processing and Technology **173**, 92-100 (2006).

[89] B. Beidokhti, A.H. Koukabi, A. Dolati., Influence of titanium and manganese on high strength low alloy SAW weld metal properties, Mat. Charact. **60**, 225-23 (2009).

[90] M.C. Zhao, Y.Y. Shan, E.R. Xiao, K. Yang, 2 Acicular ferrite formation during hot plate rolling for pipeline steels, Mater. Sci Technol. **19**, 355-359 (2003).

[91] B. Hwang, S. Lee, Y. M. Kim, N.J. Kim, J.Y. Yoo, Correlation of rolling condition, microstructure and low-temperature toughness of X70 pipeline steels, Metall. Mater. Trans. A **36**, 1793-1805 (2005).

[92] L. Sharma, R. Chhibber, Design of CaO-SiO$_2$-CaF$_2$ and CaO-SiO$_2$-Al$_2$O$_3$ based submerged arc fluxes for series of bead on plate pipeline steel welds : Effect on Carbon and Manganese content, Grain size and Microhardness, Journal of Pressure vessel Technology, ASME **141**, 1-10 (2019).

[93] S.H. Hashemi, D. Mohammadyani, Characterisation of weldment hardness, impact energy and microstructure in API X65 steel, International Journal of Pressure Vessels and Piping **98**, 8-15 (2012).

[94] E. Surian, R. de. Rissone, De. Vedia, Influence of molybdenum on ferritic high-strength SMAW all-weld-metal properties, Weld J. **84**, 53-62 (2005).

[95] G. de. Souza et al., Microstructural analysis of single pass 2.25% Cr-1.0% Mo steel weld metal with different manganese amounts. Mater Charact. **55**, 19-27 (2005).

[96] M.C. Zhao, K. Yang, F.R. Xiao, Y. Shan, Continuous cooling transformation of undeformed and deformed low carbon pipeline steels, Mater. Sci. Eng. A. **355**, 126-36 (2003).

[97] S.S. Babu, Mechanism of acicular ferrite in weld deposits, Current Opinion in Solid State and Mat. Sci. **8**, 267-278 (2004).

[98] K.L. Chang et al., Investigations of microstructure and phosphorus distribution in BOF slag, China Steel. Tech. Rep. **21**, 1-6 (2008).

[99] J.C.F. Jorge, L.F.G. Souza, J.M. ARebello, The effect of chromium on the microstructure/toughness relationship of C-Mn welds metal deposits, Mater. Charact. **47**, 195-205 (2001).

[100] B. Beidokhti, R. Pouriamanesh, Effect of Filler Metal on Mechanical Properties of HSLA steel Welds, Welding Journal **94**, 1-9 (2015).

[101] K.C. Mills, The estimation of slag properties, Southern African Pyrometallurgy **1**, 2-12 (2011).

[102] K.C. Mills, The influence of structure on the physico-chemical properties of slags. ISIJ International **33**, 148-156 (1993).

[103] T. Coetsee, F.D. Bruin, Chemical Interaction of Cr-Al-Cu Metal Powders in Aluminum-Assisted Transfer of Chromium in Submerged Arc Welding of Carbon Steel, Processes **10** (2), 296 (2022).

[104] C. Wang, Z. Wang, J. Yang, Revealing the Viscosity-Structure Relationship of SiO_2-MnO-CaO Fluxes Geared Toward High Heat Input Submerged Arc Welding, Metallurgical and Materials Transactions B **53**, 693-701 (2022).

[105] D. Nimker, R. Wattal, Zero Waste Concept: Recycling of Slag to Use as Flux in Submerged Arc Welding, Lecture Notes in Advances in Mechanical and Materials Technology, (LNME) 641-647 (2022).

[106] K.C. Mills, A.B. Fox, R.P. Thackry, Z. Li, The performance and properties of mould fluxes, VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy **1**, 1-7 (2004).

[107] M. Hayashi et al., Effect of ionicity of nonbridging oxygen ions on thermal conductivity of molten alkali silicates, Physics and Chemistry of Glasses – European Journal of Glass Science and Technology Part B **42**, 6-11 (2001).

[108] G.H. Zhang, K.C. Chou, Simple method for estimating the electrical conductivity of oxide melts with optical basicity, Metallurgical and Materials Transactions B **41**, 131-136 (2010).

[109] D. Bhandari, R. Chhibber, N. Arora, Effect of electrode coatings on diffusible hydrogen content, hardness and microstructures of the ferritic heat affected zones in bimetallic welds, Adv. Mater. Res. **383**, 4697-4701 (2012).

[110] Y. Kim, K. Morita, Relationship between Molten Oxide Structure and Thermal Conductivity in the CaO-SiO2-B2O3 System, ISIJ International **54**, 2077-2083 (2014).

[111] C. Kenneth, K.C. Mills, Structure and Properties of Slags Used in the Continuous Casting of Steel: Part 1: Conventional Mould Powders, ISIJ ISIJ International **56**, 1-13 (2016).

[112] P.J. Bray, R.V. Mulkern, E.J. Holupka, Fundametals of Mettalurgy, J. Non-Cryst. Solids **75**, 37-44 (1992).

[113] J. Zhongtang, T. Yongxing, J. Non-Cryst. Solids **146**, 57-62 (1992).

[114] Y. Waseda, J.M. Toguri, The structure and properties of oxide melts, publ. World Scientific, Singapore, (1998).

[115] S. Sridhar, K.C. Mills, Physicochemical and thermophysical behaviour of silicate slags, Ironmaking and Steelmaking **27**, 238-242 (2000).

[116] K.C. Mills, Behaviour of Slags, ISIJ Intl. **33**, 148-156 (1993).

[117] G. Eriksson, A.D. Pelton, Critical evaluation and optimization of thermodynamic properties and phase diagrams of the CaO-Al_2O_3, Al_2O_3-SiO_2 and CaO-SiO_2-Al_2O_3 systems, Met. Mater. Trans. B. **24**, 807-816 (1993).