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Introduction

1.1 OVERVIEW

The demand for petroleum products worldwide has increased due to an increase in population growth and industrial development. With a considerable increase in demand as well as an increase in natural gas and crude oil resource locations, the transportation of oil & gas is a significant issue. Transportation of petroleum products is preferred using the pipeline. Pipelines pass through various onshore as well as offshore regions by covering few to thousands of kilometers distance. More emphasis was given for the development of high strength steel for pipeline manufacturing, which can perform under severe service conditions. High strength steels and low alloy grades for low temperature service are required to provide the high strength, ductility, and toughness in pressure vessels and structures that must serve at –45°C and lower. The tensile as well as yield strength of the HSLA steel widely depends upon the crystal structure during service at low temperatures. These HSLA steels display a comparatively loss in ductility in sub-zero temperature range. To improve the low temperature ductility of metals the pipeline steels are manufactured specifically for severe service conditions.

It is an economical and safe option to use high strength pipeline materials for oil and gas industries due to high tensile strength, toughness, and specific modulus of elasticity [Mathias et al., 2013, Hashemi and Mohammadyani, 2012]. High strength low alloy steels are also known as carbon-manganese steel or low carbon steel because maximum carbon content is 0.2%, 1.5% manganese, while other alloying elements are nickel, chromium, niobium or titanium, etc. [Morrison, 2000]. The real boost in the quality of pipeline steel started in 1960 when the use of low carbon steels resulted in more robust grades. As the pipeline industry progressed, more emphasis was given for relatively small consumption and better performance of steel for long pipelines. Due to this, the potential pipeline manufacturer looked for ways of cutting costs of successive projects. The main reason for doing so was to increase the operating pressure (i.e., flow rate) and to reduce the tonnage of steel used in a pipeline [J.M. Grey, 2002]. In the 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 pipeline manufacturers to produce stronger and technically challenging steels. The most commonly used grades of pipeline steel evolved rapidly from X52 to X60 and then X65 to X70 through 1990. In 1993, a new class (X80) came to the pipeline family 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 stabilized carbon-manganese steel. It strengthened with niobium and vanadium, which had a lower ability to extend to higher strengths. For this, vanadium was replaced by molybdenum, which is strong carbide former, and the very active strengthening agent. The high effectiveness of molybdenum, along with the use of niobium, allows for durable alloy [John Piper, 2002]. With the passage of timing, the demand for line pipes in offshore transmission has increased, and with the advent in technology to manufacture pipeline steel also changed. With the advent of X70 grade to steel, it observed that the structural transformation necessary to further increase the yield strength 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. Available literature suggests that the carbon content in pipeline promotes the sensitivity towards hydrogen cracking, due to this X80 steel is more susceptible to hydrogen cracking because carbon equivalent of X80 is more as compared to lower grade steels [Paul Bilston and Milan Sarapa, 2002]. Equivalent carbon content (C.E) is used to understand how the different alloying elements affect hardness of the steel being welded. This is then directly related to hydrogen-induced cold cracking, which is the most common weld defect for steel, thus it is most commonly used to determine weldability.

$$CE_{IIW} = \%\,C + \frac{\%Mn}{6} + \frac{\%Cr+\%Mo+\%\,V}{5} + \frac{\%Cu+\%Ni}{15} \qquad (1.1) \qquad \text{[IIW formula, 1967]}$$

Various issues such as chemical composition specifications, mechanical behavior, joining, cutting, manufacturing, etc. of pipeline steels specified by the American Petroleum Institute (API) and International organization for standards (ISO). Table 1.1 shows the year of occurrence of API grade pipeline steel [Trench et al., 2001]. Table 1.2 shows the mechanical properties of various API grades.

Table 1.1: Year of occurrence of API grade pipeline steel [Trench et al., 2001]

Grade	*X42*	*X46*	*X52*	*X56*	*X60*	*X65*	*X70*	*X80*	*X90*	*X100*	*X120*
Year of occurrence	1948	1953	1953	---	1966	1967	1973	1985	1985	1985	1998

Table 1.2: Mechanical properties of various pipeline grade steels [Specification for linepipe steel, 2008]

API code	*Yield strength (MPa)*		*Tensile strength (MPa)*	
	Minimum	*Maximum*	*Minimum*	*Maximum*
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

In the present study, the material investigated is high strength low alloy (HSLA) API X70 grade pipeline steel having maximum yield strength (533MPa) and maximum ultimate tensile strength (663MPa). API X70 pipeline grade is generally carbon-manganese steel and chromium, nickel, titanium, and copper are the main alloying elements present.

Initially, electric-resistance welded or flash-welded processes were used by the manufacturer to weld pipe that provides the reliability of longitudinal seam joint. Girth electrically welded steel was also used at the same time, which brought an excellent upgrade compared to acetylene welds [J.M. Grey and John Piper, 2002]. It is essential to identify the suitable joining procedure for the welding of pipeline steel and, more importantly, the performance of the welded joint and its ability to satisfy the design load requirements during pipeline transmission. Initially, for pipeline joining manual metal arc (MMA) and gas metal arc (GMA) welding processes were used. High repairing cost occurred using conventional welding processes due to this; automated welding processes replaced these processes. Defect rates were reduced drastically with computerized processes like pulsed GMA welding and submerged arc (SAW) welding (Philip Venton, 2002). The submerged arc welding process preferably used for welding of larger thickness high strength pipeline steels [Jindal et al., 2013]. Due to the indigenous properties such as smooth surface finish, leakproof weld joints, easy control or automation, and prevention against atmospheric contamination, submerged arc welding frequently used for pipeline welding [Chai and Eagar, 1982, J.H. Palm, 1972, Bang K et al., 2009].

In submerged arc welding, the various physicochemical and thermomechanical interactions exist in the weld pool due to the slag-metal reactions. The transfer of metallic elements consists of multiple constituents, such as fluorides, oxides, or carbonates [Singer et al., 1979]. Different flux elements and oxygen disintegrate in the weld pool, due to the contribution of all oxides from the fluxes. Oxide inclusions formed when flux constituents react with oxygen and act as nucleation sites for the development of critical phases such as acicular ferrite during the submerged arc welding process. It observed in the previous literature that the presence of these phases (acicular ferrite) in the weld metal enhances the impact toughness value [Davis et al., 1991]. The physicochemical properties and chemical composition of a flux mixture depend on the raw material and have a significant effect on the penetration depth. Alkaline and alkali oxides develop the vapors that more easily ionized and thus produce a stable arc. In submerged arc welding, elemental diffusion, and heat transfer during slag-metal interactions depends upon the flux composition mixture [Singh et al., 2013 and Olson et al., 1979]. High strength pipeline steel weld poses serious problems such as low-temperature cracking and hydrogen-induced cracking. When the stress at the weld or HAZ region exceeds the ultimate tensile or shear strength of the base metal, then cracks may occur. Hydrogen induced cracking may occur due to the diffusion of hydrogen content, a higher value of hardness or coarse-grained microstructure, and very low temperature (e.g., -100° C) conditions [Plessis et al., 2007, Allen et al., 1992, Terashima et al., 1976]. To solve this problem suitable selection of submerged arc welding flux composition and filler wire is very important because flux composition plays an essential role in improving the mechanical and microstructural properties of final weld deposit [Davis et al., 1991, Bang et al., 2009, Singh et al., 2013, Jindal et al, 2013, Ana et al, 2011].

The present works aim at the development of submerged arc fluxes (for three flux systems e.g., basic, rutile basic, and rutile acidic) for welding of HSLA X70 grade pipeline steel.

Rutile, silica, silicates, clay, oxides, limestone, fluorides are the raw materials used in flux preparation. In welding flux, each raw material induces different characteristics, and varying proportion of each component gives better performance. SAW fluxes categorized according to the chemical nature of the flux, such as acidic, basic, semi-basic, or highly basic. CaO, BaO, CaF_2, MnO, K_2O, MgO, Na_2O, etc. show necessary behavior while SiO_2, TiO_2, and Al_2O_3 are acidic in nature. The chemical nature of the fluxes decides the basicity index (BI) of fluxes, and it is the ratio of the basic to acidic oxides. Physicochemical properties, as well as mechanical properties (tensile strength, hardness toughness, etc.), are affected by the BI index of fluxes.

$$BI = \frac{[CaO+MgO+CaF2+Na2O+K2O+0.5(MnO+FeO)]}{[SiO2+0.5(TiO2+Al2O3]} \qquad (1.1)\ [\text{Tuliani, 1969}]$$

Low basicity fluxes (having range of 0.5-0.9) give high current carrying capacity, good bead appearance, and good slag detachability. Excellent crack resistance behavior was observed for high basic fluxes (having range of 2.3-4.0) [Thomas et al., 1977]. Two main types of SAW fluxes are used, such as agglomerated flux and fused flux [Renwick B.G et al., 1976; Davis et al., 1977 and Chai et al., 1982,].

a) Fused fluxes:

The fused fluxes are prepared by fusing the raw ingredients in the furnace. Mostly in the industry, fused fluxes are utilized due to non-hygroscopic nature. Various minerals such as dolomite, sand, china clay, fluorspar, etc. are used for the manufacturing of fused fluxes. Grains are fine particles, free from moisture, and usually in a reddish-brown color. The main demerit of fused fluxes is that they are a little bit costlier due to more handling and processing (Campbell H. C. et al., 1957; Jackson C.E et al., 1973 & 1977).

b) Agglomerated fluxes:

These are also called ceramic fluxes and prepared by mixing raw materials with a binding agent (e.g., potassium silicate). Binder is usually used to bond the raw materials properly. In these fluxes, ferroalloy constituents such as ferromanganese, ferrosilicon, and ferrotitanium are majorly present. Gradually agglomerated fluxes are replacing fused fluxes due to lower cost in manufacturing. The main drawback of agglomerated fluxes is that they are hygroscopic. That's why it gives weld metal porosity at low moisture level. Drying of these fluxes can reduce it before use. The main advantage of agglomerated fluxes is that they are cheaper as compared to fused fluxes.

1.2 ORGANIZATION OF THE THESIS

There are total six chapters in the thesis, and breakup wise division of each chapter is given below:

The Chapter 1 (Introduction), gives the brief introduction about thesis work, brief description about pipeline steel and its applications, brief description of joining of pipeline steel, description about submerged arc welding fluxes.

The Chapter 2 (Literature Review), presents literature review of the previous work on the need of HSLA steel in Pipeline industry, brief about properties of pipeline steel, description about the role of submerged arc fluxes in weldability of pipeline steel, brief about physico-chemical behaviour of SAW fluxes and detail about effect of flux elements and welding process variables on mechanical and micro-structural properties of pipe line steel welds, discussion about effect of submerged arc welding fluxes on diffusible hydrogen and oxygen content, brief literature on flux formulation design. Identification of gaps from literature.

The Chapter 3 (Problem formulation), discusses the problem formulation and the plan of experimentation

The Chapter 4 (Experimentation) discusses about extreme vertices design for formulation of fluxes and mixture design approach for optimization of physicochemical and thermophysical properties of submerged arc fluxes, discussion about selection of welding process parameters and flux preparation, discussion about physicochemical and thermophysical characterization of SAW fluxes (For three flux systems) such as density, grain fineness number, weight change, change in enthalpy, thermal conductivity, thermal diffusivity and specific heat, contact angle and surface tension measurement method, discussion about experimental procedure of phase and structural analysis of fluxes. This chapter discusses about experimental welding set up and multi-pass bead on plate experiments using SAW fluxes such as bead chemistry, grain size and microhardness measurements, discussion about selection of suitable fluxes from three flux systems, qualitative analysis of beads based on multipass bead on plate weld deposits experimentation, discussion about submerged arc welding and various characterizations using suitable fluxes from three flux systems, discussion about experimental procedure of different characterization of weld samples (selected from three flux systems) performed using suitable fluxes, discussion about various physicochemical and thermophysical properties of submerged arc welding slag for thee flux systems, detail about experimental procedure of corrosion behaviour of X70 steel in different exposing environments.

The Chapter 5 (Results & Discussion), detail about optimization of physicochemical and thermophysical properties, Analysis and discussion for physicochemical and thermophysical responses for three flux systems. Mathematical regression modelling for density, thermal conductivity, thermal diffusivity, change in enthalpy and percentage weight change in terms of flux mixture constituents developed, analyzed and optimized for three flux systems, For three flux systems contour graphs for density, thermal conductivity, thermal diffusivity, change in enthalpy and percentage weight change were developed, Mathematical regression modelling for bead chemistry, grain size and microhardness value in terms of flux mixture constituents developed, analyzed and optimized for three flux systems, discussion about wetting and surface tension properties, Detail about bead width, height and dilution and microstructure analysis. Detail about individual and interaction effect of flux constituents on physicochemical and themophysical properties of three flux systems. Mechanical, microstructural and hydrogen induced cracking (HIC) measurements for submerged arc welded specimens. Mathematical regression modelling for density, thermal conductivity, thermal diffusivity, and specific heat in terms of slag mixture constituents developed, analyzed and optimized for three flux systems.

The Chapter 6 (Conclusion & Future scope), presents the conclusion of research work carried out in the thesis. Scope of future work is enumerated at the end of this chapter.