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RESEARCH ARTICLE

EFFECT OF FLUX COMPOSITION ON ELEMENT TRANSFER DURING SUBMERGED ARC WELDING (SAW): A LITERATURE REVIEW

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ABSTRACT

Submerged arc welding is widely used in the fabrication of pressure vessels, pipe lines and offshore structures because of its higher metal deposition rate, good strength of the joint and good surface appearance. The properties of the welded joint such as strength, toughness can be improved by controlling the microstructure of the welded joint. The element transfer from the flux has major influence on weld metal composition and weld metal properties. To predict weld metal properties, it is necessary to determine the weld composition, which primarily depends upon wire, flux, parent metal, slag metal reactions, process parameters, dilution and electrochemical reactions. Numerous investigators have attempted to determine, which flux components are of most importance in establishing the final weld chemistry. The weld chemistry is decided by the metallurgical reactions in SAW but to decide the extent of metallurgical reaction in saw is very difficult because of large variations in cycle temperature, reaction time, high heat input. In SAW due to short reaction time during SAW the reaction is not reached to its thermodynamic equilibrium, so the exact prediction of weld metal chemistry is difficult. The purpose of this literature review is to focus on an innovative approach which is needed while deciding weld chemistry. It would be worthwhile if one could develop a frame work to predict the Mn, Si, carbon, oxygen and other elements in the final weld metal, from a given combination of electrode, flux and base metal. The work done so far on Element transfer study is very limited. Much published information is not available about fluxes made by Industry professionals as they do not disclose the composition of the flux for which they claim higher strength and better mechanical properties. This literature review will provide the basis for researchers in the field of SAW.

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INTRODUCTION

Study of directions of various chemical reactions associated with weld pool and reaction products are often analyzed using principle of thermodynamics. Christensen (1949) performed the first systemic welding flux pyro metallurgical investigation in which thermodynamic concepts was applied. Various investigators (Belton *et al.*, 1963; Chai and Eagar, 1981) have used thermodynamics to predict the direction of various chemical reactions associated with the weld pool. The chemical reactions decide the final weld composition. The weld composition is governed by chemical potential of FeO, which is formed at slag metal interface. The magnitude of the chemical potential of the FeO is governed by the slag and metal compositions, equilibrium constant of the reaction and the diffusion coefficients (Natalie *et al.*, 1986; Blander and Olson, 1984). The chemical potential has strong effect on weld pool chemistry (Olson, 1989).

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The activity of FeO at the interface is higher when the activity of metal oxide in the slag is high and that of metal element in the iron alloy is low. A convenient way of studying the effect of flux composition on element transfer or weld metal chemistry is to compare the analyzed composition with that of expected composition, which can be calculated by knowing dilution, plate composition and wire composition (Tanaka *et al.*, 1980). The extent of transfer or loss of a specific element can be evaluated by a delta quantity, which is the difference between the analytical and nominal composition. These quantities indicate the influence of the flux on the element transfer during welding. A positive delta quantity indicates an elemental transfer from the flux to the weld metal, whereas negative delta quantity suggests an elemental loss from the weld pool to the slag. If the delta quantity changes rapidly with the flux composition, it is difficult to maintain the weld metal composition, microstructure and properties with small variations in flux composition. Fluxes that provide almost constant delta quantity, either positive or negative can obtain the desired weld composition by selecting the proper flux combination to compensate for the delta quantity. The

important elements that decide the weld chemistry and important mechanical properties are C, Si, Mn, O, S, Ti, B, Ni, Cr etc. Most of the researchers have studied the effect of flux composition on mechanical properties and from the properties they have interpreted the presence of various elements in weld metal (Beidokhtiet al., 2009; Dallam et al., 1985; Prashadet al., 2008). Fluxes in SAW of various steels are not readily available and flux compositions are not clear and they are patented. So the literature available for study on effect of flux composition on element transfer is very limited.

## Literature Review

Davis and Bailey (1978, 1980) revealed in their research that element transfer in SAW depends not only on its concentration in the flux but also depends upon the other substances, which are present in the flux e.g. Si transfer from the flux depends upon Al, Ti, Zr, which act as a network former and replace Si in a network leaving Si free to transfer. If the proportions of the network formers to metals or oxides in the flux is more than the transfer of Si is higher and if low the transfer is also low. Mn transfer from flux to the weld metal is also affected by the presence of Ca and Mg, because Ca, Mg and Mn ions are interdependent. Carbon is lost from the weld in most of the fluxes due to weld oxygen content. The reaction of carbon and oxygen removes carbon from the weld in most of the fluxes. Tanaka et al. (1980) studied the effect of flux composition on transfer of the elements silicon, manganese, titanium, boron and oxygen during submerged arc welding by adding simple substances titanium, boron and alloys of ferro boron, ferro titanium etc. In this study it was found that Si, Mn transfer to the weld depends not only its concentration in the flux but it was affected by the presence of Ti, Mg, Al and Ca. It was also confirmed by Davis and Bailey (1980).

MnO, SiO<sub>2</sub> added more silicon and manganese to the weld as these are weak oxides and if they are deprived of oxygen the transfer of these elements take place. This study also founded that more Ti could be transferred to the weld metal from the flux if Al, Mg are added to the flux as simple substances. Titanium transfer also depends upon the basicity index and if BI is high, Ti can be transferred easily to the weld metal even if it contains less TiO<sub>2</sub>. It is because titanium oxide is less stable than MgO and alumina, so if TiO<sub>2</sub> in the slag is deprived of oxygen by Al, Mg additions resulting Ti transfer to the weld metal, However B transfer does not depend upon BI. Ti, Mg, and Al acts as de oxidants and reduces the weld oxygen content, which increases the rate of Ti transfer to the weld. The influence of flux on weld oxygen (Tanaka et al., 1980), the oxygen potential of a flux is considered as the partition of oxygen between metal and slag and is related to FeO activity of the slag (Tanaka et al., 1980). TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have lower oxygen potential than SiO<sub>2</sub> so they produce less oxygen in the weld. Thus for oxides with high K equilibrium constant, FeO activity is significant, whereas for more stable oxides with low K value the FeO activity is lower at the interface. If the equilibrium is reached oxygen activity will be proportional to the FeO activity in the slag. The magnitude of chemical potential of FeO is governed by the slag and metal composition, the equilibrium constant for the reaction, and diffusion coefficient. This chemical potential has a strong influence on the resulting weld pool chemistry. Thier and Dring (1980) established a metallurgical model for studying element

transfer during submerged arc welding. Its application gives quantitative data for gain or loss of elements arising from slag metal or gas metal reactions during welding. The composition of metal introduced in the process can generally be changed within three zones of the process, droplet reaction, mixture of the droplets with the molten metal of the parent metal and bath reaction. From the experimental results obtained in some last year (Eagar, 1978), it was concluded that the fluxes containing less than 3% ferroalloys, the bath reaction is negligible. The calculation of the model leads to the equation.

$$X_{wn} = (1 - D^n) \times (X_E + \Delta X) + D^n \times X_P \quad (1)$$

Where X<sub>wn</sub>, concentration of element X in the wt percentage in the n<sup>th</sup> run of the weld, X<sub>E</sub> is concentration of element X in the wire electrode, X<sub>P</sub> is concentration of element X in the parent metal, X, gain or loss of element through droplet reaction, D is dilution and n is the number of runs. If the number of runs increases, the influence of parent metal decreases, with an infinite number of runs, mathematically pure weld metal is obtained.

$$X_{pwm} = \lim_{n \rightarrow \infty} X_{wn} \quad (2)$$

Combining the above two equations results in

$$X_{pwm} = X_E + \Delta x \quad (3)$$

Palm (1972) studied the effect of flux composition in element transfer study and found that various elements like Ca, Mg, Al, etc. do not directly affect the weld composition. As the equilibrium constant for these reactions is very high, so their effect on weld composition can be left out of consideration, so no traces of Ca, Mg and Al are transferred to the weld metal from the slag. The only reactions in which C, Si, Mn, S, P and O<sub>2</sub> takes part are important

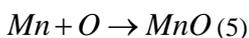
$$K_{mn} = \frac{[MnO]}{[Mn]} = \frac{[K_{si}][SiO_2]^{1/2}}{[Si]^{1/2}} \quad (4)$$

$$= \frac{K_C[Co]}{[C]} = \frac{K_{Fe}[FeO]}{[Fe]} = [O]$$

The absolute value at equilibrium not only depends upon the concentration of the elements at the start of the welding but also depends on the ratio of slag and molten metal. This later is given by the setting of the machine. This means for the same flux, wire and wire diameter, base plate, shape of seam, the final composition may differ more or less widely. The setting of machine, however have no influence on the direction of reaction, i.e., on the tendency of loss or gain of elements in the weld metal and oxide in the slag., on the other hand the direction may differ for the same flux and setting depending on the composition of wire and or base plate. It follows from the equation (4) increase of Mn in the wire leads to a higher Si and C and lower oxygen content of the weld metal. The MnO content of the slag increases the SiO<sub>2</sub> and FeO content decreases. Increase of Si in the wire also leads to a higher Mn and a lower O<sub>2</sub> content of the weld metal. The SiO<sub>2</sub> content

of the slag increases, the MnO and FeO content decreases, on the other hand increase of Mn or Si in the wire always contribute to increase of Mn and Si, however at the same time to a lower dissolved O<sub>2</sub> content of the weld metal. Fluxes containing MnO and SiO<sub>2</sub> can approach practical metallurgical neutrality; however it is possible only in a limited range of wire and base plate composition and related setting. Dissolved oxygen, Si, Mn decides the impact strength and transition temperature. Chai and Eagar (1980) and North *et al.* (1978) studied the effect of SAW parameters on weld chemistry and observed the recovery of carbon, Mn, Si and oxygen to the weld metal. The study concludes that weld chemistry primarily depends upon flux composition, but welding parameters may produce significant changes in the weld chemistry. Christensen and Chipman (1953) in a study found that weld speed has the greater effect on Mn recovery but this conclusion was contradicted by North in a similar study. Belton *et al.* (1963) found that for Si recovery during saw, the equilibrium temperature was attained but no such equilibrium was obtained for FeO reaction, while the FeO reaction is thought to control the oxygen potential of fluxes.

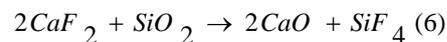
Kubli and Sharav (1961) found that less oxygen was transferred to weld while reducing the amount of SiO<sub>2</sub> and this again was confirmed by Tullianiet *al.* (1969), who showed that oxygen content in the weld metal decreases as the BI is increased. North *et al.* (1978) suggested that oxygen content was proportionate to CaO content in carbonate fluxes but this was not true for fused fluxes. Eagar (1978) introduced thermodynamic approach for the study of fluxes, on the basis of which we can predict the direction of reaction, if not the magnitude since it is difficult to reach the reaction to equilibrium state. Eagar (1978) studied the main sources of oxygen in saw and concluded that oxygen level in saw welding is controlled by SiO<sub>2</sub> decomposition in most acidic fluxes whereas the oxygen level in basic fluxes is determined by oxygen potential of the slag as given by FeO content of the slag. The CO reaction and MnO reaction also decides the oxygen level in the weld and porosity. Wright and Elliott (1973) have shown that Si is effective in suppressing the CO formation. So if the Si content of weld is above 0.10% the CO porosity is reduced, but for highly basic flux which reduces the Si level in the weld porosity becomes a problem. Christensen and Chipman (1953) found the following reaction



From the equilibrium of the above equation one can decide the direction of reaction. If the Mn % in the flux is less than the equilibrium value of MnO, then the metal will have a deoxidizing effect, and if MnO concentration in the flux is higher than equilibrium, MnO will be dissolved in weld metal and will produce more oxygen. Chai and Eagar (1973) studied the stability of various metal oxide fluxes by adding CaF<sub>2</sub> to binary fluxes, and effect of adding these oxides to pure CaF<sub>2</sub> fluxes. The study found that CaF<sub>2</sub> reduces the oxygen content in the weld metal but this is believed to be due to dilution of metal oxide rather than a direct reaction. The effect of CaF<sub>2</sub> in reducing the oxygen depends upon the stability of flux oxides. The result shows that the stability decreases in the following order.



The study shows that during saw due to temperature plasma the thermodynamic stability is changed and some more stable oxides like, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O decomposes in to sub oxides and generate more oxygen. Heile and Hill (1975) have proposed SiO as one of the source of fumes generation in gas metal arc welding. The element transfer shows that pure CaF<sub>2</sub> does not influence the Si transfer but addition of small amount of SiO<sub>2</sub> in the flux causes a significant increase in Si transfer to the weld, but if MnO is added to the flux the Si content is reduced due to oxidation of Si by MnO. Mn content in the weld increases only by addition of MnO, while other oxides MgO, K<sub>2</sub>O reduces the Mn content. SiO<sub>2</sub> addition first increases Mn content and after that the weld Mn content is reduced. The reason for the above has been given that at low concentration of SiO<sub>2</sub> tends to reduce the rate of Mn evaporation, while increasing concentration of SiO<sub>2</sub> the evaporation of Mn is increased. Others (Tullianiet *al.*, 1969; Ito *et al.*, 1976) have suggested that CaF<sub>2</sub> reduces the oxidizing potential of SiO<sub>2</sub> by the reaction.

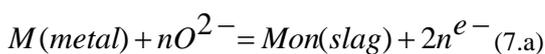


Eagar and Mitra (1991) and Mitra *et al.* (1984) developed a kinetic model to describe the transfer of alloying elements between slag and metal. For any given temperature and reaction there are neutral points at which the transfer of elements from the slag or vice versa is zero. Eagar measured the neutral points for various flux system and developed a thermodynamic model that can predict neutral points for some slag system. The study further says that the activity of oxide in the slag is not the same as that of in the flux. The slag acts as a source or a sink of alloying elements. For a particular change in weld metal or a change in flux the composition of slag changes very little. Ferrera and Olson (1975) discussed the performance of the MnO-SiO<sub>2</sub>-CaO ternary flux system and found the influence of each chemical additive on the chemical and physical properties. The above properties are related to slag viscosity, arc stability, bead shape and arc stability. Diffusion, reaction rate and heat transfer during welding depends upon viscosity of flux (Spraragen and Claussen, 1939).

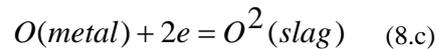
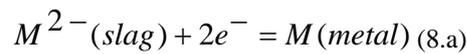
A flux with low viscosity increases the reaction rate between the metal and flux and because of it diffusion of elements between metal and slag will be rapid. So the physical properties also affect the rate of element transfer in saw. The viscosity of the flux decreases when CaO, MnO, Fe<sub>2</sub>O<sub>3</sub>, CaF<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> content is increased. The removal of S and P from the weld increases by addition of CaO. Putapov and Lynbavski (1970) have found that basic fluxes promote weld porosity and blistering on low alloy steel. Burcket *al.* (1990), studied the transfer of various elements Si, Mn, O<sub>2</sub>, Ni, Mo, and Cr by taking SiO<sub>2</sub> content as fixed and added CaF<sub>2</sub>, CaO and FeO at the expense of MnO. The oxygen transfer to the weld increases by addition of FeO because FeO is less stable than MnO, while the addition of CaO and CaF<sub>2</sub> reduces the weld oxygen content; it has been earlier explained (Chai and Eagar, 1973). Mn transfer to the weld is decreased by increasing the addition of CaF<sub>2</sub> and FeO content. This may be due to the evaporation of Mn by oxygen and due to reducing MnO but CaO addition does not affect the transfer of Mn, because the MnO activity in the slag is not affected by CaO (Kou, 2002). The Si was

transferred to the weld, Carbon content is not changed by these additions. With addition of CaO the loss of Ni, Mo and Cr from the weld occurs, while with the addition of FeO the loss of Cr and Ni occurs, without changing the Mo, but no significant change occurs with addition of CaF<sub>2</sub>. Tulianiet *al.* (1969, 1972) studied the effect of carbonate fluxes on toughness of the weld metal. High heat input in saw effects properties of weld metal. The reason for the lower toughness was the large transfer of Si and oxygen to the weld metal, when high silica or low basicity fluxes are used. In this study the purpose was to develop carbonate fluxes which in the light of oxidation and de-oxidation reactions could develop improved mechanical properties. Kanjilal *et al.* (2005) studied the effect of flux composition and welding parameters on element transfer and chemical composition. Rotatable designs based on statistical experiments were used. The fluxes were used by varying the ingredients CaO, MgO, CaF<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Variations of weld metal manganese, silicon, nickel and carbon were observed, the gain of Si and Mn is observed in electrode positive polarity due to electro chemical reactions, while loss of the above was seen on EN polarity due to oxidation of these elements. Polarity changes had no effect on sulfur and phosphorous. Carbon and nickel does not take part in electro chemical reaction but variation is seen by changing the polarity. Lower nickel is found in EN polarity, due to formation of other oxides which impede the transfer of nickel from slag or flux to weld metal. In EP polarity weld pool being cathode takes part in reduction reaction and such hindrance of nickel is restricted, therefore high Ni in electrode positive polarity is expected.

The transfer of elements was predicted by developing a quadratic model in terms of flux ingredients with the application of statistical experiments for mixture design (Kanjilal *et al.*, 2007). This study shows that element transfer in saw can be predicted with the help of regression model. It was also found that the variation of transfer of elements across the weld pool is due to chemical reactions associated with SAW fluxes at fixed level of welding parameters. Electro chemical Reactions (Polar *et al.*, 1990; Indacochea *et al.*, 1989; Kim *et al.*, 1990), Electro chemical reactions have recently been identified as important considerations in direct current welding. Kim *et al.* (1990) investigated the different chemical effects at anode and cathode. When performing DCRP welding with a silicate flux, the voltage is sufficiently high that all slag constituents could decompose electro chemically. The electrolytes involved can be from flux and or the plasma. Kim *et al.* (1990) studied the effect of electrochemical reactions on the weld metal composition in SAW and significant composition differences were observed when electrode polarity was varied in DC welding. The following anodic oxidation reactions were proposed.



These reactions occur at the electrode tip slag interface in the electrode positive polarity or the weld pool slag interface in electrode negative polarity. Therefore oxidation losses of alloying elements and pickup of oxygen are expected at the anode. The following cathodic reduction reactions were also proposed.



The reducible ions lost at the slag weld pool interface can be replenished by diffusion through the diffusion boundary. The slag composition at the boundary layer will thus have a higher concentration of ions with large diffusion coefficients than the bulk composition, consequently, low valent basic oxides will predominate and high valent acid oxides will be present at lower concentration at the interface in this diffusion limited reduction. In addition, the elemental enrichment in the weld pool can occur by weld pool- base plate exchange reactions. The concentration of elements such as carbon, sulfur, and phosphorous are higher in molten iron than in solid, so there is a tendency for transport of these elements in to the liquid across the liquid solid boundary. Thus the melting of the base plate alone can lead to compositional changes in the weld metal. Pandey *et al.* (1994) studied the effect of saw parameters and flux basicity index on the weld chemistry and transfer of elements Mn, Si, carbon and sulphur was investigated. Five fluxes were used for the study and it was found that welding current and voltage had appreciable effect on element transfer. The weld composition shows a gain of Si and loss of Mn, carbon and sulphur. The results obtained were similar as obtained by Kanjilal *et al.* (2005).

Fleck *et al.* (1986), In this study the main objective was to find the effects of filler metal wire and flux composition on transfer of Ti, B, and Mo. The experiment was repeated by using various combinations of filler wire and fluxes. The filler wire was fabricated to investigate the individual effect of Ti, B, and Mo on the weld metal transformation behavior. The oxygen transfer to the weld was also depending upon the grain size of austenite. Ti, and B, showed the reduction in the amount of N in the weld metal because of precipitation of titanium nitride Bang *et al.* (2009), in this study SAW was performed by using metal cored wire and fluxes with different compositions. The element transfer was measured and this was interpreted in terms of mechanical properties. This study reveals that basic fluxes yield less delta quantity of carbon and manganese through the reduction of oxygen content in the weld metal and due to higher Mn activity in the slag. The transfer of Si is followed by the presence of other oxides such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>.

Crespo *et al.* (2010) studied the effect of changing the BI of the flux, by making CaO additions and keeping MnO and SiO<sub>2</sub> as constant. This study reveals that more Mn can be transferred to the weld metal without changing Si, P, and S. It makes this possible to use a low Mn wire with high CaO flux and medium Mn wire with low CaO content of the flux. Ana *et al.* (2003) studied the chemical and structural characterization of fluxes used in SAW. This enables one to quantify the ions that might be present in the plasma arc due to the fluxes. On the basis of the above one can predict the reaction in the weld pool and finally the composition of the weld metal. Kumar *et al.* (2010) Developed acidic fluxes from the dust of various commercial acidic fluxes and compared the chemical

composition and mechanical properties of all the weld metal. In this study they discussed the transfer of various elements like C, Mn, Si, Cr, Mo and it was found that the composition of weld metal made by dust were in the same range as that of parent commercial fluxes. Numerous investigators (Terlikov *et al.*, 1983; Francis *et al.*, 1990; Efimenko, 1980) have reported on the chemical behavior of various welding flux systems. The FeO-MnO-SiO<sub>2</sub> system has been thoroughly investigated since it is most suitable for welding low carbon steel.

## Conclusions

Various researchers have studied the effect of flux composition on element transfer and weld metal chemistry. Different ingredients in the flux system provide the process with different pyro-metallurgical characteristics and thus different microstructure and weld metal chemistry. The weld composition does not depend only on its concentration in the flux or wire but it is also affected by the other additions or alloys which are present in the flux. To understand the weld composition, it is essential to design fluxes for a particular electrode, base plate combination with the help of ternary phase diagrams. The design methodology decides the flux composition, which should melt at approximately 50°C lower temperature than the parent metal for proper fluxing action. The weld metal composition in SAW cannot be described only on the basis of equilibrium conditions, because during SAW the temperature is so high and the process is so fast, that the equilibrium cannot be established in such a short duration. For those reactions which are having very high equilibrium constant, the reaction for these elements can be neglected e.g. elements like Ca, Mg, Al are not transferred to the weld material during SAW.

On the basis of the above literature review it can be safely inferred that weld composition is greatly influenced by flux composition and by the welding conditions. Stability of metal oxides present in the flux, network formers present in the flux, basicity index, oxidation and reduction reactions, oxygen potential of flux, FeO activity of slag, ratio of slag and molten metal, CO and MnO reactions, rate of heat input, rate of evaporation of various elements, physical and chemical properties of flux, electrochemical and thermo chemical reactions, chemical potential of the flux, physical properties of flux, chemical partitioning between slag and weld metal, electrode polarity, welding process parameters, thermodynamic and kinetic factors play an important role in determining transfer behavior of flux.

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