

SLAG-METAL REACTIONS IN SUBMERGED ARC WELDING : AN OVERVIEW

by
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INTRODUCTION

The requirements placed on welding fluxes and the resulting slag are numerous. For instance the flux and the resulting slag must be able to contribute to arc stability, weld metal alloying, weld metal deoxidation, weld metal protection, ease of slag detachability, control of inclusions due to slag entrapment, hence the resulting mechanical properties, control of porosity, facilitating welding in various positions, among others (1, 2, 3). However, these requirements can be better fulfilled only if there is a good understanding of the many reactions occurring simultaneously at the slag metal interface during welding (1). This is because there are extremely complex interconnections between the aforementioned requirements and the reactions occurring at the slag metal interface. The aim of this article, therefore, is to present a simple overview of slag-metal reactions occurring during submerged arc welding.

In general, the use of slags is limited to the welding of ferrous

materials (4) and hence the discussion presented hereafter is assumed to be for that system. Also, since there are similarities in the chemical reactions occurring between the slag and metal in welding and steelmaking (4), certain aspects of the discussion presented were taken from the steelmaking literature.

FUNDAMENTAL ASPECTS

Concept of equilibrium in slag-metal reactions

Chemical reactions may be classified as being either equilibrium or non-equilibrium reactions. Non-equilibrium reactions proceed in only one direction until one or all of the reactants are exhausted and occur in open systems; an open system is one in which mass may enter the system or be removed to the surroundings. However, equilibrium reactions are those in which the forward and backward reactions occur at the same rate and can only be achieved in a closed system; a system in which mass may not enter the system, or be removed to the surroundings (5). With respect to

chemical reactions occurring in submerged arc welding, there was, and still is, a debate regarding the occurrence of equilibrium of these reactions with many investigators having differing opinions (6). Indacochea et al stated that the achievement of equilibrium would be impossible barring in small volumes (1). The aforementioned investigators attributed this to high temperature and density gradients, presence of different phases, large electric currents and the large radiative transfer to the arc, but believe that the cautious utilization of equilibrium considerations is possible for analysis of chemical reactions and mechanisms in welding. In addition, Seferian (3), Blake (7) and Fleming et. al. (8) also agree that equilibrium is not achieved during welding. However, Chai and Eager (9) have proposed a thermodynamic model for treating the equilibria between metal and slag during submerged arc welding and most investigators choose to adopt the concept of effective equilibrium temperature; which is the temperature at which the equilibrium composition of the

reaction system becomes identical to the actual weld composition after welding(10).

Equilibrium of reactions occurring between the slag and metal was first proposed by Bojko (11). Fitch proposed that thermodynamic equilibrium may be reached locally on the basis that the short time duration is compensated for by the high temperatures and high surface-to-volume ratio (12). Other investigators such as Babcock (13), Bischof (14), Christensen (15) and Claussen (16) later made methodical measurements and concluded on the basis of their data that high temperature equilibrium was achieved. Nevertheless, the analysis of chemical reactions between the metal and slag will be made simpler if equilibrium or at least effective equilibrium is assumed to have been achieved. This would then allow the application of thermodynamic models to slag-metal reactions.

Application of thermodynamic models to slag-metal reactions

Application of thermodynamics to slag-metal reactions allows analyses such as the determination of the weld metal composition to be made. This however, requires the assumption of equilibria of the slag-metal reactions and hence, the adoption of the effective equilibrium temperature concept by most investigators as stated above. With the assumption of effective equilibria the use of the

well-known concepts of Law of Mass Action and activities can then be justified (3). Using these two concepts the equilibrium constants and the partition of chemical species between the slag and the weld metal may then be determined.

The most often-cited thermodynamic model of slag-metal reaction in the literature is the one proposed by Chai and Eager (9). The above two concepts were made use of by them to develop a model for slag-metal reactions during submerged arc welding (9). It has been proposed that the basicity index (BI), of submerged arc welding fluxes is given by the following term (9,17) :

$$BI = \frac{CaO + MgO + SrO + Na_2O + K_2O + Li_2O + \frac{1}{2} (MnO + FeO)}{SiO_2 + \frac{1}{2} (Al_2O_3 + TiO_2 + ZrO_2)}$$

However, this definition of basicity index is similar to those given by Tuliani et. al. (18) and Siewert and Ferree (19) except the omission of CaF_2 . In the model proposed by Chai and Eager (9), the equations involved, for SiO_2 , include :

$$SiO_2 (liq) = [\%Si] + 2[\%O]$$

$$\log K = - \frac{28360}{T} + 10.61$$

$$K = \frac{a_{Si} \times a^{2O}}{a_{SiO_2}}$$

Using the last equation given above and **Fig. 1** below, the activity of SiO_2 in the slag may be calculated as a function of basicity index. The activity coefficient of SiO_2 at 2000°C was then obtained using existing data at 1600°C and extrapolation to 2000°C allowing the concentration of SiO_2 in the flux to be plotted against basicity index. Similarly, other species such as MnO may be studied.

This thermodynamic model proposed by Chai and Eager, which was studied by Mitra et. al. (20), predicts the Mn and Si content in the resulting weld after submerged arc welding using commercial fluxes. The model was found to be as successful in predicting the Mn content of weld metal as most other empirical approaches, but for Si gave values significantly different from those determined experimentally.

Nevertheless, the generality of the approach and the scientific basis on which it is founded makes the model more useful and credible for the determination of submerged arc welding deposits.

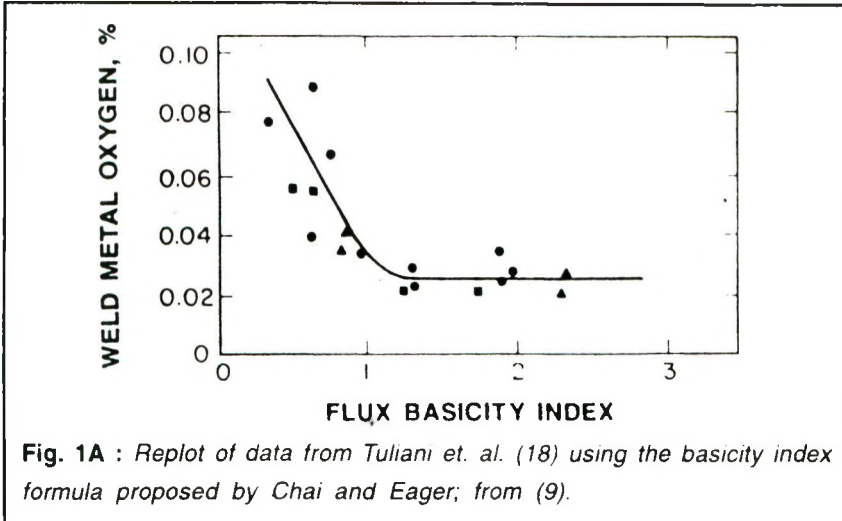


Fig. 1A : Replot of data from Tuliani et. al. (18) using the basicity index formula proposed by Chai and Eager; from (9).

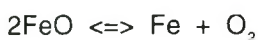
Slag-metal reactions in submerged arc welding

As has been stated earlier, slag-metal reactions are highly complex processes. Hence, in this section only a few well-known reactions will be addressed; namely the overall reactions involving oxygen, hydrogen, sulphur and phosphorus, silicon and manganese.

Reactions involving oxygen

Reactions involving oxygen have been studied both by steelmakers and in welding (2,21,22). Ferrous oxide is only soluble in iron to a certain extent and beyond this point, it would remain undissolved.

This means that the ferrous oxide will be partitioned between the slag and the metal (21). In addition, the maximum solubility of oxygen in iron increases with temperature (23). The equation for the reaction is as follows :



$$K = \frac{[\text{O}]}{(\text{FeO})}$$

where, [O] denotes oxygen concentration in the molten iron and the (FeO) the free oxide content of the slag. The chemical equation stated above suggests that the uptake of oxygen may be controlled by the FeO composition at the interface and was proposed so by Indacochea et. al. (1). However, this was refuted by Chai and Eager (9) in their analysis which had considered only the bulk composition of FeO. The value of K depends on the type of slag, whether acidic or basic, and was given as a function of time by Korber and Oelsen(24).

Davis and Bailey (2), based on their studies of steelmaking slags, proposed the following relation :

$$K = \frac{\text{Fe}^{2+}}{A(\text{O}^{2-})^{1/2}}$$

where A is a constant. This

relation, however, was found to be not applicable for acidic slags and was attributed to the sharing of the oxygen atoms in polymerized species such as SiO_4^{4-} , AlO_3^{2-} and TiO_4^{4-} . Nevertheless, Davis and Bailey (2) have proposed the use of the following ratio as an indicator to the degree of polymerization :

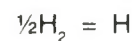
$$\frac{(\text{Fe}^{2+} + \text{Mn}^{2+})}{\text{Ca}^{2+}}$$

The above ratio may then be used to calculate the (O^{2-}) and hence predict the oxygen level in the weld(2).

Reactions involving hydrogen

Submerged arc welding fluxes may be classified, on the basis of method of manufacturing, in three types - namely fused, bonded and agglomerated. Evans and Baach (25) have stated that only the agglomerated types may have residual moisture content and hence are prone to producing welds of high hydrogen levels.

In liquid iron, the solution of hydrogen follows Sieverts Law (6,21) and the chemical equation is as follows :



$$K = \frac{[\text{H}]}{(\text{P}_{\text{H}_2})^{1/2}}$$

The equilibrium constant, K, has been given as a function of temperature by Seferian (21). Also, Seferian has stated that the Fe-H system was influenced by oxides such as FeO and MnO

with the solubility of hydrogen in the metal being reduced with an increase in FeO content for a particular temperature, the welding speed as well as the presence of oxides (21). Studying the effect of oxides, Reeve (26) proposed that the influence of FeO may be quantified by the following relation:

$$[\text{FeO}] \times H_D = 0.18.$$

Where, H_D is the diffusible hydrogen. However, the estimation of the hydrogen content in the weld metal is difficult; being a function of time (21).

Reactions involving sulphur and phosphorus

Welding fluxes may also be used for the removal or control of sulphur and phosphorus content of the weld metal; the capacity of welding fluxes to assume this function is unclear with only the lime rich fluxes being able to perform this(4). This is similar to the function of slag in steelmaking(4). However, the slag itself may contain very small amounts of sulphur and phosphorus and hence impart inaccuracy to any attempt at analysis (2). Nevertheless, Hatch and Chipman (27) have developed a parameter called the 'excess base' for blast furnace slags, given as :

$$\text{Excess Base} = X_{\text{CaO}} + A X_{\text{MgO}} - X_{\text{SiO}_2} - X_{\text{Al}_2\text{O}_3}$$

where A is a constant and X_{CaO}

X_{MgO} , X_{SiO_2} and $X_{\text{Al}_2\text{O}_3}$ are mole fractions of the CaO, MgO, SiO₂ and Al₂O₃ in the slag. The excess base has been shown to be related to sulphur partition for welding slags (2).

The behaviour of phosphorus in submerged arc welding, however, may not be as easily dealt with using reaction equations from steelmaking. Davis and Bailey (2) attributed this to relatively smaller amounts of phosphorus in submerged arc welding and the fact that the phosphorus oxidation reaction of slag components was not taken into account in the equations.

Reactions involving manganese

Manganese has been suggested to form inclusions, such as iron-manganese silicates ((Mn, Fe)SiO₃), iron-manganese oxides ((FeMn)O) and galaxite (MnO.Al₂O₃), which contribute to the toughness (7, 8). Hence, the manganese content must be controlled for the achievement of optimal properties. This requires an understanding of reactions involving manganese at the slag-metal interface.

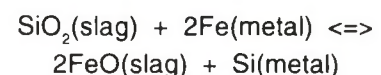
Coe and Davis (28) described the partitioning of manganese in steelmaking slags by the relation

$$\log K_{\text{Mn}} = \frac{\log X_{\text{MnO}} [\text{Mn}]}{X_{\text{FeO}}} = \frac{7406}{T} - 3436$$

However, the reciprocal relationship between $\log K_{\text{Mn}}$ and $\log \text{Mn}$ implied by the above relation does not hold true for welding fluxes. Bailey and Davis (2) plotted $\log K_{\text{Mn}}$ against $\log (x\text{CaO} + x\text{MgO})$ and found sufficient consistency in trend. These investigators attributed this to the fact that the interdependence of activities between CaO, MgO and MnO may 'in some way' determine the partitioning of Mn between the slag and weld metal. Chai and Eager (9), taking a scientific approach, had proposed their thermodynamic model which is applicable to partitioning of Mn and has been applied so by Mitra et. al. (20). This model has given very good agreement between the predicted and experimentally determined values of Mn content.

Reactions involving silicon

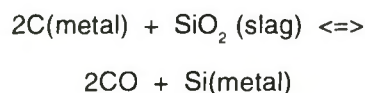
The reaction equation between metal and slag may be written as:



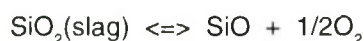
Assuming equilibrium and applying the Law of Mass Action to the above equation, it may be said that the silicon content would be inversely affected by the FeO content. However, Indacochea et. al. (1) had studied the partition of silicon between slag and metal in submerged arc welding and reported that there was an increase of silicon in the weld metal even though the FeO content was increasing. This

unexpected result was attributed by them to two possibilities. However, in both possibilities, the diffusion of SiO₂ is slow at lower temperatures. In the first case, the investigators proposed that the diffusion of SiO₂ is the rate limiting factor above 2100°C and hence there would be a steady mass transport of SiO₂ to the slag-metal interface.

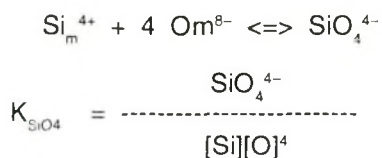
The second case proposed by them involves the reaction (1) :



The above reaction may be less plausible as it involves the formation of a gaseous product which is difficult to nucleate in view of the high surface and interfacial tensions expected of silicates and iron. However, they proposed that these barriers may be overcome when the metal contacts the gaseous plasma which is at equilibrium with the slag through reactions such as (1) :



Davis and Bailey considered the deoxidation of silicon (2) :



A major advantage of this analysis would be to eliminate the need to have values of (O²⁻). Hatch and Chipman (27) had plotted the relationship between log K_{SiO₄} against log [O] and

obtained a gradient of 4, lending more credibility to this analysis.

Concluding Remarks

The study of slag-metal reactions is far from being comprehensive. There is still a considerable gap in our understanding of this complex phenomenon although scientific models such as that proposed by Chai and Eager (9) have extended our ability to predict reactions somewhat. Nevertheless, entrenched empirical approaches which gave acceptable results continue, justifiably to be used by some researchers.

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