

Technical Note

How Fluxes Determine the Metallurgical Properties of Submerged Arc Welds

Dissolved oxygen, the deciding factor in determining impact properties—in particular the transition temperature—is controlled by the molten slag and its active components

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ABSTRACT. From metallurgical considerations it is concluded that the dissolved O-content (and not the total O-content) of the weld metal very likely is the decisive factor determining its impact properties, especially its transition temperature.

The dissolved O-content depends on the O-potential of the surrounding active medium. In submerged arc welding this is the molten slag and its active components; as far as O is concerned, this is practically restricted to SiO_2 , MnO and FeO .

Basic components can only chemically bind the acid oxide SiO_2 , but not the apparently amphoteric oxides MnO and FeO . Basicity therefore only governs the part played in the O-activity by SiO_2 . Though very important in this respect it fundamentally is (contrary to general opinion) a factor of secondary order only. This means that the metallurgical quality of a flux can at most partly be represented by basicity formula.

Acid, Neutral or Basic

In papers and lectures on welding fluxes one nearly always finds the opinion that the main factor governing the mechanical properties of weld metal, especially its impact behavior, is basicity. However, in general any acceptable explanation is missing.

Moreover, the authors fail in distinguishing between metallurgical and chemical factors and in a certain sense a lack of understanding in this matter seems obvious.

This is particularly true as far as the meaning of the word neutral is concerned. It therefore seems justified to go somewhat closer into this and related matters.

Properties of Fluxes in Molten State

In the several phases of the welding process the molten flux must possess certain physical properties which are decisive for their application. For example, these properties concern the melting and solidification range, the viscosity range, current capacity, arc

stability, speed capacity, shape and appearance of the weld and slag detachability. This means that the concentration of the constituents must be restricted between certain limits.

In general, the flux constituents are oxides like MnO , SiO_2 , CaO , MgO , Al_2O_3 , TiO_2 and Na_2O and fluorides like CaF_2 and Na_3AlF_6 . In the case of sintered or agglomerated fluxes they may also contain deoxidizers and alloying elements.

As we shall elucidate later on, SiO_2 is seldom required from a metallurgical point of view; however, it must be added to obtain the necessary viscosity and current capacity. A high CaO content is required for chemical and, indirectly, metallurgical reasons. CaO also improves arc stability. However, beyond certain limits also determined by the other constituents, it makes the viscosity of the slag too low.

It also makes the flux more sensitive to moisture pick-up which is liable to cause porosity. MgO has a similar effect and Al_2O_3 also increases the sensitivity to moisture. MnO favors high

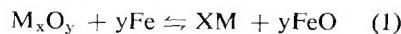
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welding speed and deep penetration and decreases the sensitivity to rust and porosity. On the other hand it decreases the current capacity.

Metallurgical Properties of Molten Flux

The preceding arguments set limits to the metallurgical properties, which concern the interactions between molten slag and molten weld metal, the latter being made up from a mixture of molten wire and molten base metal.

In general this interaction can be represented by



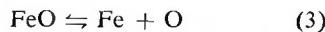
in which M_xO_y may be any metal (or other oxide in the slag) and M is the corresponding element dissolved in the molten metal. The reactions in any case must thermodynamically endeavour to reach equilibrium conditions and equilibrium will therefore be more or less approached.

The summarized equilibrium conditions of (1) are:

$$K_m \frac{[M_xO_y]^{1/y}}{[M]^{x/y}} = K_{Fe} \frac{[FeO]}{[Fe]} = K_{Fe} [FeO] \quad (2)$$

In which M_xO_y and FeO are the concentrations of these oxides in the slag and M and Fe the concentrations of those elements dissolved in the weld metal at the moment that equilibrium is established, i.e. the reactions have come to their theoretical end. K_m is a constant depending on the temperature only. Since the weld metal comprises of iron with at the most a few percent of other elements, Fe may be regarded as equal to one.

Also the reaction:



takes place and tends towards equilibrium

$$K_{Fe} \frac{[FeO]}{[Fe]} = K_{Fe} [FeO] = [O] \quad (4)$$

in which $[O]$ is the concentration of dissolved atomic O in the weld metal at equilibrium.

Taking the presence of C in the weld metal into account one has:



with the corresponding equilibrium:

$$K_c \frac{[CO]}{[C]} = K_c \frac{\geq 1}{[C]} = [O] \quad (6)$$

CO may be the concentration or pressure of developing CO which approaches 1 under atmospheric conditions. (Due to surface tension effects the CO pressure may be substantially over 1 atm during the interaction.)

From the preceding considerations it

follows that via the corresponding reactions the tendency is to arrive at the equilibria

$$\begin{aligned} K_{Ca} \frac{[CaO]}{[CA]} &= K_{Mg} \frac{[MgO]}{[Mg]} = \\ K_{Al} \frac{[Al_2O_3]^{1/3}}{[Al]^{2/3}} &= K_{Mn} \frac{[MnO]}{[Mn]} \\ = K_{Si} \frac{[SiO_2]^{1/2}}{[Si]^{1/2}} &= K_{Fe} [FeO] = \\ K_C \frac{\geq 1}{[C]} &= [O] \end{aligned} \quad (7a)$$

It is true that our assumption that the constants are only dependent on the temperature of the slag-metal melt is not quantitatively correct. In fact this is only true on application of the thermodynamic activities instead of the concentrations of the constituents.

These quantities differ more or less due to mutual physical and chemical effects of the constituents, but for a qualitative approach to the direction of the reactions, its application seems to be sufficiently justified. This is particularly valid for a given flux where during the welding process the changes of concentrations in the flux and the absolute concentrations of the elements in the weld metal are small.

In 7a the constants K_{Ca} , K_{Mg} , K_{Al} (and also, K_{Li} , K_{Sr} , K_{Ba} , K_{Ti} , a.o. if necessary to consider) are so extremely high that the corresponding reactions can be left completely out of consideration. This means that practically no trace of Ca, Mg, Al, etc. is transferred from the slag to the metal. In other words only the reactions in which Mn, Si, C and Fe take part are of practical importance and decisive for the eventual composition of the weld metal.

Hence (7a) may be simplified to:

$$K_{Mn} = \frac{[MnO]}{[MO]} = K_{Si} \frac{[SiO_2]^{1/2}}{[Si]^{1/2}} = K_{Fe} [FeO] = K_C \frac{\geq 1}{[C]} \quad (7)$$

The absolute values arrived at equilibrium not only depend on the concentrations at the start of welding, but also on the ratio of slag and molten metal.

The latter is in its turn given by the setting of the welding machine (current, voltage and speed). This means that even for the same flux, wire and wire diameter, base metal, thickness of base metal and shape of the seam, the final composition may differ more or less widely. The settings of the machine, however, have no influence on the direction of the reactions, i.e. on the tendency to loss or gain of the elements in the weld metal and the oxides in the slag.

On the other hand the direction may differ for the same flux and setting, depending on the composition of the wire and/or the base metal. Evaluation of

gain or loss of Mn and Si for a given flux as such is therefore rather meaningless. It can be done only for the flux in combination with a given wire, base metal and quantitatively only in combination with a certain setting of machine parameters.

It now follows from (7) that, under otherwise constant conditions and assuming all mentioned components are present in the molten phases;

1. Increase of MnO in the flux leads to a higher final SiO_2 and FeO concentration in the slag and a higher Mn and O and a lower Si and C content of the weld metal (and vice versa).

2. Increase of SiO_2 in the flux leads to a higher final MnO and FeO concentration in the slag and a higher Si and O and a lower Mn and C content in the weld metal.

3. Increase of MnO and SiO_2 simultaneously will, depending on their ratio, generally lead to an increase of Mn and Si in the weld metal simultaneously, though beyond or below extreme ratios Si or Mn may decrease. O always increases, while C always decreases.

It also follows from (7) that: (1) increase of Mn in the wire leads also to a higher Si and C and a lower O content of the weld metal. The MnO content of the slag increases the SiO_2 and FeO content decreases; increase of Si in the wire also leads to a higher Mn and C and a lower O content of the weld metal. The SiO_2 content of the slag increases, the MnO and FeO content decreases.

Summarizing, we find that increase of MnO and/or SiO_2 always contribute to increase of Mn + Si and at the same time to a *higher dissolved O content* of the weld metal.

On the other hand increase of Mn and/or Si in the wire also always contribute to increase of Mn + Si, however, at the same time to a *lower dissolved O content* of the weld metal. Equal Mn and Si content in the weld metal can therefore be obtained at different O levels.

It is generally accepted that Si as an alloying element in the weld metal does not favor impact properties, particularly the transition temperature. The same is also very probably true for Mn.

Dissolved O definitely seems to have a disastrous influence on impact strength. This a.o. is confirmed by the high impact values and low transition temperature of extremely pure iron, made under vacuum. The apparently favorable role of limited amounts of Mn and Si under practical conditions finds its reason only in the reduction of dissolved O during the phases of the welding process where slag and metal are no longer strongly intermixed. Interaction between slag and metal then comes to an end.

In the liquid and the solid state of

the metal too, reactions strive for corresponding equilibria. This results in binding of a part of the dissolved O under formation of secondary slag-particles in the liquid and finely dispersed tertiary particles in the solid weld metal by the corresponding elements.

At equal contents of Mn and/or Si a lower dissolved O content in the liquid weld metal consequently results in a lower dissolved O content of the solid weld metal at atmospheric temperature.

From the metallurgical point of view it is therefore desirable that the flux has the lowest possible MnO and SiO₂ content. This flux approaches *ideal metallurgical neutrality* in the most complete way, which means that independently of the composition of wire and base metal the change of composition of molten wire plus base metal is limited to a minimum. Fluxes containing MnO and/or SiO₂ can approach a *practical metallurgical neutrality*, which means that none or little difference exists in Mn and Si content of weld metal calculated from the geometry of the weld only and weld metal at equilibrium conditions. However, this is only possible in a limited range of wire and base metal compositions and related settings. Under all conditions where the flux is not metallurgically neutral in relation to the weld metal, the final composition of the latter differs more or less from that calculated from wire composition, plate composition and dilution. This means that loss or gain of the elements in the weld metal occurs. On repeated welding on the preceding weld metal, losses or gains accumulate asymptotically, i.e. in a decreasing degree to a finite content, where the flux becomes ideally metallurgically neutral for the weld metal.

Flux/wire combinations for a given base metal resulting in strong losses or gains per run are therefore not suitable for multi-run welding. Under practical conditions there is nearly always some loss in C and a gain in Si.

Apart from those cases where silicon is required as an alloying element (strength in higher tensile steels) it can be regarded as unwanted. Application of wire having more than a trace up to 0.15% Si is therefore an exception.

Though the majority of fluxes lead to a gain of Mn, some types lead to rather high losses. Consequently wires with corresponding Mn content in a range of 0.5 to 2.0% or even more have to be used.

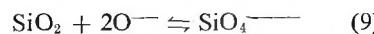
Chemical Properties of Fluxes in Molten State

The several oxides present in the flux may vary from more or less strongly basic via chemically neutral to less or

more strongly acid in character. Basic oxides are characterised by their tendency to split off O⁻ ions e.g.



Acid oxides on the contrary bind available (free) O⁻ ions e.g.



The chemically neutral (amphoteric) oxides can do both, depending on the composition of the slag as a whole, but to a small degree only. These chemical reactions also proceed to corresponding equilibria. An oxide is now regarded as more strongly basic the more O⁻ ions are split off at the same total concentration of the oxide. As an oxide becomes more strongly acid, more O⁻ ions are bonded. In molten fluxes CaO is almost completely dissociated i.e. behaves in a very strongly basic fashion, while SiO₂ behaves in a very strongly acidic fashion.

The consequence is that as far as O⁻ ions are available SiO₂ is almost fully bonded to SiO₄⁴⁻.

Moreover SiO₄⁴⁻ ions tend on their turn to bind SiO₂ molecules to complexes. The consequence of the presence of basic oxides therefore is that a corresponding part of the SiO₂-concentration becomes metallurgically inactive. In other words the flux gets the properties of a flux of lower SiO₂ content and behaves metallurgically in that way. Though CaO, as has been elucidated in the preceding chapter, does not directly take part in the metallurgical reactions, it indirectly has a strong influence on these reactions through chemical binding of SiO₂. The binding to SiO₄⁴⁻ is nearly complete at the mol. ratio CaO/SiO₂=2 (chemically the formula of Ca₂SiO₄, Caorthosilicate), which differs only little from the corresponding weight ratio. Higher ratios have therefore a minor effect only, which is in accordance with experience on impact behavior.

Like CaO, BaO and the alkali oxides are strongly basic. As far as other oxides are concerned MgO is usually regarded as rather strongly basic, but apparently behaves less basic than CaO. This means that a much higher MgO/SiO₂ ratio is needed to obtain a similar result. Al₂O₃ is amphoteric. In the steel industry it is even regarded as weakly acid.

Due to a lack of understanding of the real meaning of its important metallurgical role, MnO is usually also regarded as rather strongly basic. However, it is, like FeO chemically amphoteric too. This already follows from the experience that in fluxes its metallurgical activity seems hardly or not be influenced, neither by CaO nor by SiO₂.

Basicity Formulas

It follows from the preceding considerations that the primary factor for

the weld metal is the O-activity. It also follows that the O-activity is only partially influenced by the basicity which only governs that part of the O-activity given by SiO₂.

It is therefore not justified to believe that the properties of a flux, as far as composition and mechanical properties of the weld metal are concerned, may be fully characterised by a basicity formula, of which many exist.

As far as there is any need for such a formula of secondary order it should neither contain amphoteric or very weak oxides like MnO, FeO, Al₂O₃, TiO₂ a.o. nor CaF₂ which is an almost fully dissociated neutral compound in the molten flux.

Dissolved Oxygen Affects Impact Properties

One can hardly omit to conclude from the foregoing reasoning that dissolved O is a very important if not the decisive factor in determining impact properties. Obviously this theory is sustained by several facts.

It is a general experience that with decreasing acidity, i.e. decreasing O content these properties improve and vice versa. Also that beyond the ratio CaO/SiO₂ = 2, the improvement is of a lower order.

Steel made under vacuum generally has very good impact properties. This is especially true for very pure iron molten in vacuum. Additions of strongly deoxidizing elements like Al, C_a, Mo and others in amounts that have still no appreciable alloying effects, generally improve impact properties.

It is on the other hand obvious that in welding and steelmaking under oxides with high O activity (MnO, FeO, dead soft electrodes) the impact properties are extremely low.

It is true that one can wonder whether dissolved O, which under all conditions can be present only in extremely small amounts, has such a tremendous influence on impact properties.

However, it should be realized that the same can be said with respect to similar small amounts of C and N which are proven to be responsible for the yield phenomenon, strain aging, blue brittleness and elastic after-effect in mild steel.

References

This paper is based on the following papers in which the ion theory was applied on fluxes and the dissolved O theory was put forward.

1. Report, 4th Orientation day, Automatic Welding. Nov. 1963, p. 5.
2. Discussions, Welding Symposium, Ned. Ver. Lastechniek Nov. 1964, p. 26.
3. Dissolved Oxygen in Weld Metal, Lastechniek 11 1, 1965, p. 211.
4. Automatic Welding Under Flux. Het Ingenieursblad, 1966 no. 3, p. 116.
5. I.I.W. Doc. XII-B-11-1966 and XII-A-33-71.