Prediction of Weld Metal Hydrogen Levels Obtained Under Test Conditions

Calculations based on a model agree with actual measurements and shed new light on hydrogen absorption

BY B. CHEW

SUMMARY. Using an approach based on chemical thermodynamics an expression is derived which relates weld metal hydrogen concentration, as determined by standard test methods, to the composition of the flux covering in manual shielded metal arc welding. It is shown that for certain published data agreement between the values found and those predicted can be achieved if an effective reaction temperature of 2300 C is assumed. This result, lying close to the temperature for maximum solubility in iron, suggests that hydrogen contents determined in the standard manner define the upper limit of hydrogen concentration that a particular welding rod can generate.

Introduction

When covered electrodes for manual shielded metal arc welding are used, hydrogen is inevitably produced during the process. Part of this gas enters the weld metal and diffuses outward into the components being joined. As a result, metallurgically susceptible regions of the weld can become embrittled. For this reason preheat and postheat treatments may be specified in certain cases aimed at expelling hydrogen and reducing thereby the risk of cracking.

Clearly, it would be advantageous to minimize the quantity of hydrogen generated originally and to this end several of the factors affecting the transfer of hydrogen to the weld have been identified on an empirical basis (Ref. 1). However, the nature of the underlying chemical mechanism by which this transfer occurs has not been well established although several authors (Refs. 2-4) have shown a correlation to exist between moisture in coverings and weld metal hydrogen content. Thus, the major source of hydrogen appears to be chemically bound water in the flux covering which, upon release and decomposition at high temperatures, produces the hydrogen subsequently taken up by the weld metal. In quantitative terms it is not clear why only a few percent of the total hydrogen available actually appears in the weld metal. For example, a typical hydrogen concentration determined according to one of the standard procedures (Refs. 5, 6) might be 10 ml NTP/100 g weld metal, whereas a calculation based on a 1% moisture level in the covering would indicate about 600 ml NTP/100 g weld metal to be potentially available.

The aim of the present work was to develop a model for the transfer process to account quantitatively for the concentrations obtained and, by so doing, to illuminate the mechanism of hydrogen absorption. The only progress made in this direction so far has been the calculation of weld metal hydrogen concentrations from a closed chamber analysis of the gases evolved during the actual welding operation (Ref. 7). The approach used here is somewhat different: it is to predict hydrogen contents from a prior knowledge of the electrode covering composition since this is a direct and easily determined property of the electrode itself whereas the constitution of the arc atmosphere is very difficult to measure.

Theoretical Approach

Basis of Treatment

The treatment adopted is to interpret the available data by a straightforward application of chemical thermodynamics, the advantage being that tabulated free energy and other data are available in the literature. It has to be pointed out, however, that this is essentially an equilibrium approach applied to a system which is non-isothermal and of relatively short duration, and therefore might be expected not to conform to this condition. In applying this approach to the welding situation it is assumed that the kinetic processes occur with such rapidity that chemical equilibrium is indeed attained. It is also implied that subsequent measurements on materials cooled to room temperature correspond to the 'frozen' equilibrium state achieved at high temperatures. What follows is an attempt to see how this simple equilibrium approach can explain the hydrogen concentrations found in welds deposited under standard test conditions.

Flux Decomposition

Many reactions occur simultaneously in the welding atmosphere but on the assumption that chemical equilibrium is reached in the system it is permissible to select the reaction of particular interest and treat it individually in terms of its equilibrium constant. In predicting hydrogen contents the following equation is used:

\[ \frac{1}{2} \text{H}_2 \leftrightarrow [\text{H}] \]  

(1)

for which the equilibrium constant, K', is obtained from tables of standard free energy change, ΔG°, and the relationship

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Square brackets in equation (1) denote a dissolved phase and curved brackets a gaseous one; $a_h$ is the activity of dissolved hydrogen, equal to the product of concentration and activity coefficient. $P_h$ is the partial pressure of hydrogen in equilibrium with molten metal.

The problem is one of calculating $P_h$ for which the gaseous composition of the welding atmosphere must be predicted. Considering the major components of a typical flux formulation, reference to thermodynamic data (Ref. 8) shows that the partial pressures of oxygen in equilibrium with SiO₂, Al₂O₃, TiO₂, CaO (from CaCO₃), MgO (from MgCO₃), and Al₂O₃ with SiO₂, are all, for example, $< 10^{-3}$ atm, up to temperatures in excess of approximately 2,000°C. This simply states in effect that these compounds are extremely stable and do not decompose easily. By contrast, the temperatures at which the dissociation pressure of CO₂ in equilibrium with the compounds CaCO₃ and MgCO₃ exceeds 1 atm may be calculated as about 850°C and 400°C, respectively (Ref. 9). Since the temperatures involved in welding must exceed the melting point of iron (1535°C), these compounds will decompose with extreme ease.

Another way of viewing this is to observe that a CO₂ pressure of about $10^{-3}$ atm would be required at 1535°C to prevent the decomposition of CaCO₃. Similarly, the sodium silicate used as a flux binder is known to release freely its available water at temperatures in excess of about 450°C (Ref. 10). The other major component to be considered is calcium fluoride, CaF₂. Again, calculation shows that the dissociation pressure of fluorine in equilibrium with CaF₂ at temperatures up to the melting point (approx. 1,400°C) is about $10^{-29}$ atm indicating great stability. In addition, the vapor pressure of this compound, although greater than that of the oxides present, would be only of the order of $10^{-8}$ atm in the pure state at 1400°C. In summary, then, the major contribution of the flux to the gaseous atmosphere over the weld will be in the form of CO₂ and H₂O and, to develop the model, the remaining components present may be taken as being nonvolatile.

In order to predict a composition for the welding atmosphere based entirely on that of the flux covering it is necessary to estimate first the quantity of gas liberated per unit length of weld laid. Clearly, if there were insuffi-

cient gaseous material produced to effectively shield the weld from the external atmosphere then the composition of the latter would need to be taken into account.

An examination of the flux (or slag) compositions for basic electrodes (Ref. 11) shows them to contain concentrations of CaCO₃ ranging approximately from 25-50% with an average of about 30%. Taking a representative welding speed as 1.5 cm of electrode used for every 1.0 cm traveled, then the quantity of flux consumed would be about 0.75 g, based on a mean value of 0.50 g flux/cm of electrode, which was obtained by stripping the coating from samples of nine commercial and experimental gauge 8 basic electrodes. Thus, for a flux covering containing 30% CaCO₃ complete decomposition of this component would yield about 50 m NTP of CO₂ per cm of weld laid. The actual volume of CO₂ will be greater than this since its average temperature will be well above 0°C. This is a considerable quantity of gas to be released over an area of say 1 cm² (taking the weld bead to be about 1 cm wide) being many times the volume of arc swept out and, in principle at least, more than adequate to effectively shield the weld from the external atmosphere.

It is helpful to compare the CO₂ flow-rate, in terms of the volume released per second; with that employed in CO₂ welding. Assuming the manual electrode moves at a speed of 3 mm/sec (Ref. 4) then about 1 l/min of CO₂ is being produced. Remembering that the cross-sectional area of the 8 gauge electrode is approximately 0.3 cm² and that of a CO₂ nozzle may be about 3 cm², then the manually shielded metal-arc gas flow-rate is equivalent to some 10 l/min if the comparison is made over the same area of 3 cm². This flow rate is close to the optimum for best shielding found for a particular nozzle in a recent study. (Ref. 12).

A flux containing 1% moisture would release 9 ml NTP water vapor under the same conditions of electrode consumption. Thus, the model is of a weld being laid under a blanket of CO₂ containing a certain quantity of water vapor.

Formulation of Model

In view of the quantity of gas evolved it is not certain whether all or only part of this gas mixture is actually involved in chemical reaction, or even whether all of the CaCO₃ available in the flux decomposes. In the case of manual shielded metal-arc welding the decomposition of all available CaCO₃ is probably achieved, but this would certainly not be the case, for example, in submerged arc welding with basic fluxes where the flux is present in large excess. It will be assumed in general that a fraction $k$ of the total number of moles of potentially available gas mixture actually enters the reaction zone so that $k$ may be $< 1$. If the total number of moles H₂O available per 100 g of flux is $n_w$ then $k_n w$ take part in the reaction. Let there be present at equilibrium x moles of H₂ in the gas phase which have come only from the water vapor present, so that in the following reaction

$$\text{(H}_2\text{O)} \rightleftharpoons \text{(H}_2\text{)} + \text{[O]} \quad (4)$$

we have present at equilibrium ($k_n w w$) moles H₂O, x moles H₂, and $a_w$ moles dissolved oxygen.

The dissolved oxygen content, or strictly activity, is given as an unknown $a_w$ since it cannot be calculated simply from the original H₂O content because of the additional sources of oxygen that are present. The equilibrium constant, $K$, for this reaction is given by

$$K = \frac{P_H a_w}{P_w} \quad (5)$$

and since, at constant temperature and volume, partial pressures are proportional to numbers of moles present, we can substitute moles present at equilibrium to give

$$K = \frac{x a_w}{n_w - x} \quad (6)$$

or

$$x = \frac{K n_w}{a_w + K} \quad (7)$$

If there are also $n_a$ moles CaCO₃ initially in 100 g flux then there will be $n_a$ moles CO₂ potentially available on decomposition. Since the same fraction $k$ of these is involved in reaction, and furthermore if some decomposition of this CO₂ occurs according to the reaction

$$\text{(CO}_2\text{)} \rightleftharpoons \text{(CO)} + \text{[O]} \quad (8)$$

then at equilibrium there are present ($k_n w w - y$) moles CO₂, y moles CO, and again $a_w$ moles dissolved oxygen. The total number of moles present in the gas phase is ($n_a - y$) + y + ($k_n w - x$) + x ignoring the number of moles of gaseous oxygen in equilibrium with $a_w$% in solution. This may be justified by observing that the calculated partial pressure of oxygen in equilibrium with, for example, 0.15% oxygen dissolved in pure iron at 1900°C is of the order of $10^{-8}$ atm.
The contribution of any metallic elements present to the number of moles in the gas phase, arising from their vapor pressure will be ignored also. This assumption is valid as long as the reaction temperature is well removed from the boiling point of these elements, or, if this is not so, then they are present in such quantities as to generate only small partial pressures. For the case of low alloy weld metal the element present in large excess is, of course, iron which has a boiling point of about 3,000 C.

The partial pressure of hydrogen is given by,

\[
P_H = \frac{\text{No of moles hydrogen}}{\text{total No. of moles present}} \times P
\]

where \( P \) is the total pressure of the gas mixture. Inserting equation (6) and the total number of moles above gives,

\[
P_H = \frac{K n_w}{a_o + K} \cdot \frac{P}{n_c + n_w}
\]

If the flux contains \( C_c \) wt % CaCO\(_3\) and \( C_w \) wt % H\(_2\)O then dividing by the appropriate molecular weights \( n_c = C_c / 100 \) and \( n_w = C_w / 18 \) moles per 100 gm flux. In terms of wt % equation (9) becomes

\[
P_H = \frac{100 \text{ KCW}}{P/K(18C_c + 100C_w)} + a_o(18C_c + 100C_w)
\]

Finally, substitution of equation (10) into equation (3) gives

\[
a_H = K\left[100\text{KCW}P/K(18C_c + 100C_w) + a_o(18C_c + 100C_w)\right]^{1/2}
\]

Two aspects of this result are worthy of note. The first concerns the absence of the factor \( K \), the fraction of potentially available gas mixture that actually reacts. This result is perhaps to be expected because it is the partial pressure of hydrogen in the gas phase that governs the molten metal content rather than the total quantity of hydrogen actually produced. The second aspect is the prediction that the hydrogen concentration is virtually independent of dissolved oxygen concentration when in equation (11) \( K(18C_c + 100C_w) >> a_o(18C_c + 100C_w) \), i.e., if \( K >> a_o \).

Under these circumstances equation (11) becomes

\[
a_H \approx K\left[100C_wP/18C_c + 100C_w\right]^{1/2}
\]

Further discussion in this point will be postponed until the following section which deals with the application of equations (11) and (12) to some experimental data.

**Comparison with Published Data**

In a review publication by Moreton, Parker & Jenkins (Ref. 4) the measurement of hydrogen contents in welding is described and discussed. Data have been compiled also giving weld hydrogen concentrations as a function of flux moisture contents for manual metal-arc welds. Both quantities had been determined according to standardized procedures. Those electrodes for which flux moisture, acid-released CO\(_2\) and weld metal hydrogen concentrations were all given are reproduced in Table 1. In the Table the acid-released CO\(_2\) figures have been converted also to weight per cent of “equivalent CaCO\(_3\)”, to allow direct insertion into equations (11) or (12). The possibility that some of this CO\(_2\) may not actually have come from CaCO\(_3\) does not affect the calculation which is concerned, strictly, only with the total quantity of CO\(_2\) available. The variation in moisture and hydrogen levels for certain of the electrodes results from the variety of baking treatments applied to the electrodes before welding.

In the absence of information on the weld metal oxygen contents there is the choice of using either equation (12), that is assuming \( K >> a_o \), or equation (11) and inserting an estimated figure for the oxygen content. In most cases \( a_o \) will lie between the limits 0.01 and 0.1%. Thus initially, it is assumed that \( a_o = 0.1\% \) to determine whether the condition \( K >> a_o \) is in fact fulfilled. If this is the case then equation (12) will be adequate for most purposes.

Since there is a known variation in the “equivalent CaCO\(_3\)”, figures appearing in Table 1 a direct plot of moisture versus hydrogen content would not be appropriate. It is necessary instead to compare individual values of \( a_H \), as predicted by equation (11) taking \( a_o = 0.1\% \) and \( P = 1 \text{ atm} \), with those actually found. Values of \( K' \) and \( K \) at 100 C intervals were calculated from free energy data available in the literature (Ref. 13), and the resulting hydrogen concentrations were then compared with those observed. The method of comparison was to plot ‘observed’ against ‘predicted’ in the form shown in Fig. 1 where the line drawn defines the locus of perfect coincidence between the two.

As judged by eye a temperature of 2300 C was found to give the best fit between the values observed and those predicted and this comparison is the one reproduced in the diagram. Also shown is the effect of a change of \( \pm 100 \text{ C} \) on the predicted hydrogen contents at the extremes of the range considered. Thus, 2300 C is the effective equilibrium temperature predicted for the gas/weld metal reactions under consideration. The activity coefficient for dissolved hydrogen was taken as unity in view of the high temperature and low concentrations involved, and because of lack of precision in the available free energy information. An estimate of the experimental errors on the hydrogen measurements is shown in Fig. 1 in terms of the average \( \pm 2\sigma \) limits observed at Marchwood Engineering Laboratories on hydrogen levels determined using the methods described by Moreton et al (Ref. 4).

The value of \( K \) at 2300 C is 2.69 so that compared with the assumed oxygen content of 0.1% the ratio \( K: a_o \) is about 27.1. Thus, \( a_o \) is insensitive to the oxygen content and for the degree of precision involved \( a_o \) could have been ignored allowing equation (12) to be used.

There are some further measurements quoted in the review by Moreton et al (Ref. 4) that can be used in the present work. These arose out of an international cooperative effort under the auspices of the International Institute of Welding to compare flux moisture and weld metal hydrogen levels generated by three electrodes as measured in different laboratories. The results quoted here are those obtained in Japan, Norway and Great Britain for which both moisture and hydrogen contents were reported.

Equation (12) has been used to draw up theoretical curves of \( a_H \) versus moisture content and these are compared on Fig. 2 with the results given. No carbonate figures were available for the electrodes but they are thought to be of the basic low-hydrogen type (Ref. 15). Consequently the predicted values are given as a band of results lying between 30 and 50% CaCO\(_3\) at a temperature of 2300 C. This band also serves to illustrate the effect of CaCO\(_3\) level, or more strictly the welding atmosphere CO\(_2\) content, on the \( a_H \) values. Also plotted are the values from Fig. 1 for those electrodes whose carbonate contents (Table 1) fell within the...
Predicted weld metal hydrogen level, ml NTP/100 g

chosen limits together with some data pertaining to a low-hydrogen 6 swg E11018-M electrode given in a recent paper by Hart and Watkinson (Ref. 16). In spite of considerable vertical scatter in the results there is a reasonable agreement with the predicted band both in quantitative terms and in the general form of the data.

Discussion

The temperature of 2300 °C which accounts best for the observations is somewhat high when compared with some of the figures derived from slag/metal reaction studies. Thus Christensen & Chipman (Ref. 17) measured temperatures in the range 1900-2100 °C using thermocouples embedded in mild steel plate. If, however, the reactions of interest here occur on the molten electrode tip or on the droplets as they traverse the gap between electrode and base plate, then thermocouple temperatures could be too low. Other workers finding an effective reaction temperature of about 2000 °C are Belton, Moore, and Tankins (Ref. 18) who studied the distribution of silicon and oxygen between metal and slag in submerged arc welding. However, Pollard & Milner (Ref. 19) studying the reactions occurring in CO₂ shielded arc welding, a process which is analogous in some ways to the present situation, calculated a mean effective reaction temperature of 2300 °C in close agreement with the result obtained here.

The agreement between observed and predicted hydrogen contents found here has an interesting consequence concerning the maximum hydrogen concentration that the weld metal can attain. The measured values were obtained according to either the BS1719 or IIW standard procedures both of which give similar results on the same electrode (Ref. 20). These values would tend to be too low rather than too high, due to the possible escape of hydrogen during and immediately after welding before the test piece is quenched to room temperature.

It has been shown theoretically, however, (Ref. 21) that due to the dilution of the welding atmosphere with metal vapor there is a temperature for maximum solubility at any given hydrogen partial pressure. In the case of iron this temperature is 2400 °C, close to the figure of 2300 °C found here, and this effectively puts an upper limit on the values of aH that legitimately can be predicted. Thus, it appears that the values found in practice correspond very nearly to the maximum possible at any particular partial pressure of hydrogen and consequently little hydrogen could have been lost before quenching. The implication then is that the BS or IIW tests define quantitatively an upper limit of weld metal hydrogen concentration for the particular electrode tested. Assuming this original concentration, it ought to be possible to estimate the hydrogen concentration after given periods of time at selected temperatures for a particular weld geometry either in an approximate manner as proposed by Coe & Moreton (Ref. 22) or more rigorously using analogies with heat flow theory.

Another point of interest is that the present work implies that the external atmosphere is excluded from the welding atmosphere in manual shielded metal-arc welding with electrodes containing > 16% equivalent CaCO₃. Thus no variation in hydrogen level would be expected due to variations in atmospheric humidity. This agrees with the results of tests performed by Blombery & Corderoy (Ref. 23) in which tests were made at 23 °C with relative humidities of 10% and 90%. Finally, it is interesting to note that the electrode used by these workers was stated to be "... representative of its class, i.e., rutile coated general purpose mild steel (AS B130-217) ...": They obtained mean values of 34.7 and 36.6 ml/100g. These values have been inserted into Fig. 1 and good agreement is obtained by using the average CO₂ and moisture figures given in Table 1 for the two rutile type electrodes listed there. Thus, although the formulae given above have been applied mainly to basic electrodes there is some indication that equations (11) and (12) may be applicable also to rutile coated electrodes. Clearly, this must depend on there being a sufficient quantity of metal carbonates in the flux to generate the
necessary CO₂ atmosphere for shielding purposes.

Conclusions

1. The application of simple chemical thermodynamics to certain gas/metal reactions occurring in manual shielded metal-arc welding yields a relationship, based on the flux composition, which is able to account quantitatively for the weld metal hydrogen levels that are obtained using the standard test procedures.

The coincidence of theory with practice indicates an effective reaction temperature of 2300°C.

2. The standard test methods for obtaining diffusible hydrogen contents appear to give a value which is close to the maximum that is theoretically possible for a given electrode having a particular flux moisture and carbonate content.

3. The theory predicts that weld metal oxygen concentration, at the levels normally encountered, will have only a small effect on the concentration of hydrogen appearing in the weld metal.

4. In so far as the model developed is able to account for the observed results, this justifies a basic assumption that the quantity of shielding gas produced when using electrodes whose coating contains >16% CaCO₃ excludes the external atmosphere during welding. Consequently atmospheric humidity will not affect hydrogen absorption at the time of welding.

<table>
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<th>Electrode type</th>
<th>Gauge no.</th>
<th>Code</th>
<th>Acid-released CO₂, wt %</th>
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<th>Dried 1 hr @ 450°C</th>
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Table 1 — Weld Metal Hydrogen, Flux Moisture and CO₂, Data Taken from Moreton, Parker, & Jenkins (Ref. 4)

Weld metal hydrogen, mean of 3 tests, ml/H₂NTP/100g weld metal

(a) 1 h r @ 150°C
(b) single determination.
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References