THE PART PLAYED BY OXYGEN AND NITROGEN IN ARC-WELDING

by J. D. FAST

The action of oxygen and nitrogen on iron and steel is dealt with here at some length as an introduction to an article that will follow in which the function of the coating of welding electrodes will be analysed. This article is devoted to an estimation of the solubility of oxygen and nitrogen in liquid as well as in solid iron and to a discussion of the harmful and the useful effects of these elements in electric welding. As harmful effects are discussed the causation of porosity and the adverse influence upon mechanical strength, whilst the useful effects discussed are the promotion of transfer of heat and transport of the metal across the arc. This leads to a discussion also of the part played by the reaction between oxygen and carbon.

When welding by the commonly applied method of Slavianoff an arc is struck between the workpiece to be welded and a metal rod called the electrode. The latter gradually melts during the welding and thus functions not only as electrode but also as filler rod.

At first no steps were taken to protect the molten metal against the attack of the oxygen and the nitrogen in the air, with the result that very poor quality welds were obtained. When unprotected rods of mild steel containing for instance 0.1% C, 0.1% Si and 0.4% Mn are used it is found that in the transfer of the metal to the workpiece the content of these elements is greatly reduced by oxidation. On the other hand the originally very small content of oxygen and nitrogen is increased to something like 0.15% N and 0.25% O, as a chemical analysis of the bead shows. Accordingly a microscopic examination of the deposited metal may show the presence of a considerable quantity of oxide and nitride. Furthermore, there appear to be a number of cavities in the metal due to the formation of carbon monoxide through oxidation of the carbon contained in the steel and, as will be demonstrated, also to the release of nitrogen during the cooling and solidifying of the metal.

In order to obtain welds with satisfactory mechanical properties it is therefore essential to protect the metal against the attack of oxygen and nitrogen while being transferred from the electrode to the workpiece.

In principle the simplest way to provide such a protection is to carry out the welding in a gas that is absolutely free of components which react with iron. Welding in hydrogen for instance has become well-known; use is thereby made of the large quantity of heat released by the recombination of the atomic hydrogen formed in the arc. This method, however, is a rather expensive one and is consequently used only in special cases. The same applies to welding in helium and argon, as recently developed.

A more economical protection is obtained by coating the electrodes with substances which during the welding process keep the oxygen and nitrogen away from the metal, either by the development of large quantities of other gases (organic substances) or by the formation of a sealing slag on the metal (mineral substances). Frequently a combination of both these processes is applied.

In our next article we shall go fully into the protection afforded by a slag, but first of all it is necessary to study more closely the effect of oxygen and nitrogen on iron and steel, as will be done in this article. The obsolete method of welding with bare electrodes will only be referred to in so far as it will help to give a better understanding of the part played by the coating.

We shall concentrate our attention particularly upon the questions that are of importance in the technique of welding, viz:

a) The solubility of oxygen and nitrogen in liquid iron between its melting point and boiling point; this gives us an idea of the maximum quantities that may be absorbed while welding.

b) The solubility of oxygen and nitrogen in solid iron, particularly alpha iron (the form of iron which is stable below 910 °C and is body-centred cubic); this helps to gain an insight into the effect of these elements upon the mechanical properties of welds.

c) The chemical reaction between oxygen and carbon dissolved in liquid iron; this reaction is apt to cause porosity in the welds and, what is still more important, provides the propelling force for the transfer of the metal from the electrode to the workpiece.

The injurious as well as the useful effects of oxygen and nitrogen in the welding process will be discussed in the latter part of this article.
The iron-oxygen system

Solubility of oxygen in liquid and in solid iron

If liquid iron is attacked by oxygen and the pressure of the oxygen exceeds a certain value then all the metal will be gradually transformed into liquid oxide. This can be read from the partial constitutional diagram of the iron-oxygen system (fig. 1), when it is borne in mind that to each percentage of oxygen and each temperature there corresponds a certain partial pressure of the oxygen.

Let us suppose that while maintaining a constant temperature (say 1600 °C) we cause the oxygen pressure above the liquid iron to rise gradually from zero. The state of saturation, indicated in the diagram by the solubility curve $BB'$, will then be reached already at a very low oxygen pressure. At 1600 °C this pressure is about $10^{-3}$ atm. As soon as the state of saturation has been reached, then, in addition to the liquid metallic phase, a liquid oxide phase begins to form, the composition of which is given by the position of the line $CC'$. According to Gibbs' phase rule the pressure should remain constant (about $10^{-8}$ atm.) until all the metal has been transformed into this oxide phase.

If the number of independent components in a system is $C$ and the number of phases $P$ then according to Gibbs' phase rule the number of variables (degrees of freedom) $F$ required to determine fully the state of the system is given by $F = C - P + 2$. In the case in question for the area bounded on the left and right by the lines $BB'$ and $CC'$ we therefore have $F = 2 - 3 + 2 = 1$. Consequently in this area the state of the system is a function of only one variable, e.g. the pressure or the temperature. If we take the temperature for this variable then the pressure is a function only of the temperature. Consequently, when the value of the temperature is fixed, as we have done in this case by supposing the temperature to be constant at 1600 °C, then also the pressure is fixed.

If at the constant temperature of 1600 °C the pressure of the oxygen is caused to rise further, then the liquid oxide, the composition of which on the line $CC'$ was not far removed from the stoichiometric composition FeO, gradually absorbs more oxygen. Finally at a pressure of one atmosphere an oxygen content is reached which is already greater than that corresponding to the formula FeO.

In electric arc welding with bare electrodes the reaction time is so short that actually not all the metal is transformed into oxide, as is required by the thermodynamic equilibrium, but only a partial oxidation takes place. Immediately underneath the electrode a molten mass is formed, called the pool, consisting of a metallic phase containing oxygen and covered by a thin layer of liquid oxide. At the interface the compositions of these two phases will be as represented by the lines $BB'$ and $CC'$ in fig. 1. The average composition of the metallic phase, however, will be given by points a little to the left of $BB'$ and of the oxide phase by points a little to the right of $CC'$.

What is of particular importance in welding technique is the position of the line $BB'$, i.e. the solubility of oxygen (or FeO) in liquid iron as a function of the temperature. For the temperature range between 1800 °K and 2083 °K this solubility has been accurately determined by Chipman and Fetters.

It is highly important to know the solubility also at higher temperatures, for there are indications that while passing from the electrode to the work-piece the metal is in many cases heated to the boiling point of iron. According to most experimental data the boiling point of iron lies somewhere between 2700 and 2800 °K.

By means of a few simple hypotheses regarding the thermal effect and the change in entropy taking place when liquid Fe is homogeneously mixed with liquid FeO, the following relation between solubility and temperature can be deduced:

$$T = \frac{C}{R} \ln \frac{1 - 2x}{1 - x}$$

1) According to some investigators the line $CC'$ lies to the left of the composition FeO whilst others place it to the right.
2) Of course the solubility can be expressed in % FeO as well as in % O.
The absolute temperature and \( x \) the solubility of FeO expressed as a molecular fraction, i.e. the number of molecules of FeO in the saturated solution divided by the total number of molecules. \( R \) is the gas constant and \( C \) a constant that has to be determined experimentally.

Formula (1) indicates that when plotting \( (1-2x) / \log \left( \frac{(1-x)}{x} \right) \) as a function of \( T \) we should obtain a straight line through the origin. As shown in fig. 2, Chipman’s and Fetters’ measurements satisfy this requirement quite well. The straight line in the diagram has been drawn in such a way as to point precisely towards the invisible origin at \( 0 \)°K. From its slope we find for the constant \( C \) in (1) the value

\[
C = 18300 \text{ cal.}
\]

The satisfactory agreement between theory and experiment encourages us to use equation (1) also for calculating the solubility at higher temperatures. These (calculated) solubilities can be read directly from fig. 2.

The solubility of oxygen in solid iron is so small that it could not be determined experimentally. In fig. 1 the solubility curve coincides with the \( t \)-axis.

**Absorption of oxygen when welding with bare electrodes**

Since the boiling point of iron lies at about 2750 °K, from fig. 2 it may be expected that when welding with bare electrodes the molten metal will always contain less than 1.2\% of oxygen.

Of interest in this connection are the experiments carried out by Losana\(^5\). He used bare electrodes of different diameters and made of different kinds of steel. It was found that both the oxygen and the nitrogen content of the deposited metal increased as the thickness of the electrode decreased. In not a single experiment was a content found lower than 0.14\% \( O \), or higher than 0.953\% \( O \). The results of these experiments, therefore, are not in contradiction with fig. 2.

As an example taken from a series of experiments by Losana we give in table I the C, Mn, Si, P, S, O and N contents of the metal deposited from electrodes containing 0.10\% C, 0.89\% Mn, 0.17\% Si, 0.015\% P and 0.021\% S (the balance being Fe).

**Table I. Composition of the metal deposited in some of Losana’s experiments\(^6\) when welding with bare electrodes containing 0.10\% C, 0.89\% Mn, 0.17\% Si, 0.015\% P and 0.021\% S.**

<table>
<thead>
<tr>
<th>Wire dia. mm</th>
<th>C %</th>
<th>Mn %</th>
<th>Si %</th>
<th>P %</th>
<th>S %</th>
<th>O %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>0.720</td>
<td>0.218</td>
</tr>
<tr>
<td>2</td>
<td>0.026</td>
<td>0.054</td>
<td>0.039</td>
<td>0.010</td>
<td>0.019</td>
<td>0.550</td>
<td>0.180</td>
</tr>
<tr>
<td>4</td>
<td>0.048</td>
<td>0.070</td>
<td>0.053</td>
<td>0.014</td>
<td>0.021</td>
<td>0.302</td>
<td>0.130</td>
</tr>
<tr>
<td>6</td>
<td>0.068</td>
<td>0.124</td>
<td>0.058</td>
<td>0.014</td>
<td>0.022</td>
<td>0.140</td>
<td>0.105</td>
</tr>
</tbody>
</table>

For a more exact comparison with the theory the experiments should have been carried out with wire of pure iron. In the experiments referred to C, Mn and Si were, it is true, oxidized to a considerable extent but by no means completely.

The drop in the oxygen content with increasing diameter of the electrode wire is probably related to the fact that the thicker the wire the larger are the droplets of metal transferred from the electrode to the workpiece. It may be that consequently the temperature of the metal crossing the arc is lower when thicker rods are used. Moreover, we have to take into account the fact that there is no time for the equilibrium of dissolution and the chemical equilibria to adjust themselves fully. In the following section we shall see from the example of the reaction between oxygen and carbon that these equilibria are in fact unable to adjust themselves in the process of welding.

**The reaction between oxygen and carbon in electric arc welding**

To a liquid iron phase containing small quantities of C and FeO (or O) in solution, in the state of

\(^5\) L. Losana, Metallurgia Italiana 26, 391-403, 1934.
equilibrium there belongs a gas phase consisting of a mixture of CO and CO$_2$. The reactions that can take place between the components in the two phases are the following:

\[
[\text{FeO}] + [\text{C}] \nRightarrow [\text{Fe}] + \text{CO} \quad (2)
\]
\[
2[\text{FeO}] + [\text{C}] \nRightarrow 2[\text{Fe}] + \text{CO}_2 \quad (3)
\]
\[
[\text{FeO}] + \text{CO} \nRightarrow [\text{Fe}] + \text{CO}_2 \quad (4)
\]
\[
[\text{C}] + \text{CO}_2 \nRightarrow 2 \text{CO} \quad (5)
\]

where the brackets indicate the components of the homogeneous liquid phase. Two of these equations, however, are sufficient to describe the equilibrium between the liquid and the gaseous phases, since (4) is the difference between (3) and (2), and (5) is equal to twice (2) less (3).

With the aid of thermodynamics and experimental data taken from literature it is possible to calculate the positions of the said equilibria as functions of the temperature of the steel (see the article quoted in footnote 4). Without going into these calculations we give here in table II the equilibrium pressures of CO and CO$_2$ which should correspond to the C and O contents of the deposited metal given in table I. The calculations have been carried out for two temperatures, viz: 2300 °K and 2700 °K.

<table>
<thead>
<tr>
<th>% C</th>
<th>% O</th>
<th>2300 °K</th>
<th>2700 °K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P$_{\text{CO}}$</td>
<td>P$_{\text{CO}_2}$</td>
</tr>
<tr>
<td>0.026</td>
<td>0.550</td>
<td>10.4</td>
<td>1.23</td>
</tr>
<tr>
<td>0.048</td>
<td>0.302</td>
<td>11.3</td>
<td>0.79</td>
</tr>
<tr>
<td>0.068</td>
<td>0.140</td>
<td>7.7</td>
<td>0.26</td>
</tr>
</tbody>
</table>

The choice of 2300 °K as lowest temperature is due to the fact that the highest oxygen content of deposited metal in table I of which also the C content is known is 0.55%, which according to fig. 2 would correspond already to a temperature of about 2250 °K of the metal being transferred if the equilibrium between liquid iron and liquid ferro-oxide had indeed been established during the deposition process. The actual temperature was probably higher.

In the calculations which led to the pressures given in table II extrapolations were employed which may have caused errors of 10% in the results. This, however, does not detract from the conclusion obviously to be drawn from table II that when welding with bare electrodes conditions are far removed from the state of chemical equilibrium. The (CO + CO$_2$)-pressure cannot in actual fact have amounted to more than a fraction of one atmosphere.

This failure to reach states of equilibrium will prove to be of essential importance also when dealing with coated electrodes.

The iron-nitrogen system

**Dissociation pressure of iron nitride**

When iron was attacked by oxygen at high temperatures saturated solutions were obtained, as shown above, at O$_2$-pressures far below the partial pressure of this gas in the air. In the case of nitrogen the reverse is found: at high temperatures the state of saturation both for liquid and for solid iron is reached only at N$_2$-pressures far above the partial pressure of nitrogen in air. Consequently it has not yet been possible to reach the saturation concentrations for liquid iron. As we shall see farther on, it has however been possible to determine the concentrations corresponding to a nitrogen pressure of 1 atm.

For alpha iron it was possible to reach the condition of saturation by an artifice. Instead of N$_2$, mixtures of NH$_3$ and H$_2$ were caused to react with iron. As soon as the limit of solubility is exceeded a new phase is formed (the nitride Fe$_3$N), the dissociation pressures of which at various temperatures naturally correspond to the equilibrium pressures of the saturated solutions of nitrogen in iron. As we shall see below, these dissociation pressures can be calculated and will enable us to compute an upper limit for the solubility of nitrogen in alpha iron. We shall also see (table III) that more direct determinations of the position of the solubility line AC diagrammatically represented in fig. 3 give greatly divergent values.

The explanation why NH$_3$ is so much more active than N$_2$ lies in the fact that the equilibrium

\[
8 \text{Fe} + 2 \text{NH}_3 \nRightarrow 2 \text{Fe}_3\text{N} + 3 \text{H}_2 \quad (6)
\]

is reached comparatively quickly, whereas the reactions

\[
\text{N}_2 + 3 \text{H}_2 \nRightarrow 2 \text{NH}_3 \quad (7)
\]

and

\[
2 \text{Fe}_3\text{N} \nRightarrow 8 \text{Fe} + \text{N}_2 \quad (8)
\]

take place but very slowly. If, for instance, NH$_3$ is heated for a long time to 500 °C it dissociates almost entirely into hydrogen and nitrogen, since the...
stoichiometric gas mixture in the state of equilibrium at 500 ºC and 1 atm contains only 0.12 vol % NH₃. When, however, iron is heated to 500 ºC in a stream of NH₃ + H₂ the velocity of the gas can

![Diagram](image)

Fig. 3. Part of the constitutional diagram of the iron-nitrogen system represented diagrammatically. Here α and γ indicate respectively alpha iron and gamma iron. The solubility curve of nitrogen in solid iron is given by the lines CA and BD.

easily be chosen such that the percentage of NH₃ drops only very little. The iron then reacts with a mixture of NH₃ and H₂, which corresponds to very high nitrogen pressures in the state of equilibrium. By way of illustration, the constant of the reaction (7)

\[
K_{NH} = \frac{P^2_{NH}}{P_{H_2} \cdot P_{H_2}}
\]

at 500 ºC amounts to 1.5·10⁻⁵. A gas mixture comprising 70 vol % NH₃ + 30 vol % H₂ of 1 atm thus corresponds at 500 ºC to a nitrogen pressure

\[
P_{N_2} = \frac{10^5 \cdot (0.7)^2}{1.5 \cdot (0.3)^2} = 1.2 \cdot 10^6 \text{ atm},
\]

whilst a mixture of 98 % NH₃ + 2 % H₂ corresponds even to a nitrogen pressure of about 8·10⁶ atm ⁷.

When mixtures of NH₃ and H₂ of varying composition are passed over iron at 500 ºC then the formation of Fe₄N begins as soon as the NH₃ content falls below 20 vol %.

Place in the opposite direction as soon as the NH₃ content falls below 20 vol %. If we now substitute \( P_{H_2} = 0.8 \) and \( P_{NH} = 0.2 \) in (9) then we find that \( P_{N_2} \approx 5200 \) atm. Considering (7) and (8) this means that also the dissociation pressure of Fe₄N in equilibrium with Fe amounts to about 5200 atm N₂ at 500 ºC.

In the same way we can determine the dissociation pressure for other temperatures, and from the experimental data available we deduce the following relation between the dissociation pressure of Fe₄N (in equilibrium with Fe) and the absolute temperature:

\[
\log p = -\frac{1760}{T} + 5.99 \ldots \ldots (10)
\]

According to this formula the dissociation pressure at 20 ºC is already about 1 atm. The Fe₄N needles in steel, so well known in metallography, should, therefore, dissociate spontaneously; the fact that they continue to exist is due only to the inertia of this dissociation. It is the same as with iron carbide (cementite) Fe₃C, which in iron-carbon alloys should really dissociate spontaneously into iron and graphite but only does so at an imperceptibly low rate.

Solubility of nitrogen in solid iron

Some research workers understand by the solubility of nitrogen in iron something different from what we have understood it to be in the foregoing, in conformity with the conventional definition ⁸). They understand it to be the amount of nitrogen contained in the metal in equilibrium with nitrogen of 1 atm. We have seen, however, that the true solubility say at 500 ºC corresponds to a pressure of about 5200 atm. Now in order to be able to speak about the solubility at a certain nitrogen pressure without causing confusion we shall from now onwards call the (true) solubility as indicated in the constitutional diagram of fig. 3 by the lines CA and BD the maximum solubility.

Reliable data in respect to the solubility of nitrogen in solid iron are only available for a pressure of 1 atm. They are given by Sieverts and his collaborators ⁹) and are represented by fig. 4.

According to Sieverts the solubility in alpha iron is 0.002 wt % at 890 ºC and 0.0004 wt % at 750 ºC. At these relatively low temperatures equilibrium is established so slowly that the values given

⁷) Of course these figures are not exact, because equation (9) only strictly applies as long as the gases behave as ideal gases. It would be better to substitute "nitrogen activity" for "nitrogen pressure".

⁸) This reads: solubility is the maximum quantity that can be absorbed without a new phase beginning to form.

are less reliable than those for gamma and delta iron (see note 6). Now the iron atoms in alpha as well as in delta iron form a body-centred cubic lattice and it is therefore to be expected that one continuous curve

\[ \%N_t = 0.0004 \sqrt{P_{N}} \]

\[
\begin{array}{cccc}
800 & 1000 & 1200 & 1400 \\
0.028 & 0.024 & 0.020 & 0.016 \\
0.012 & 0.008 & 0.004 & 0.002 \\
0.0004 & 0.0008 & 0.0012 & 0.0016 \\
\end{array}
\]

Fig. 4. Solubility of nitrogen in iron at 1 atm nitrogen pressure as function of the temperature. The curves drawn for solid iron correspond to the measurements of Sieverts and his collaborators (see footnote 8) and for liquid iron to the measurements of Kootz (see note 14). It is to be noted that for liquid iron various investigators find different values. For instance according to Chipman and Mutphy (Trans. A.I.M.E. 116, 179-196, 1935) the solubility immediately above the melting point is about 10% lower and according to Sieverts about 30% lower.

can be drawn through the points of alpha and delta iron. This does indeed prove to be the case (see dotted line in fig. 4) and it makes the points for alpha iron more reliable. According to fig. 4 the solubility in the gamma phase, stable between 910 °C and 1400 °C, and the solubility in liquid iron are much greater than that in alpha (delta) iron.

Now in order to be able to say something about the maximum solubilities on the grounds of these experimental data, we shall avail ourselves of the fact that the concentration of a bi-atomic gas in a metal is in general approximately proportional to the square root of the pressure.

From the example of nitrogen this can be realized as follows. The reaction constant \( K \) of the dissociation \( N_2 \rightarrow 2N \) in the gas phase is given by

\[ K = \frac{P_{N}^2}{P_{N_2}} \]

The pressure of the atomic nitrogen \( P_N \) is thus proportional to the square root of that of the molecular nitrogen \( P_{N_2} \). The nitrogen is dissolved in the metal in the atomic state and, since its concentration in iron is small, it will be proportional to \( P_N \) and thus also to \( \sqrt{P_{N_2}} \). Here, at not very high temperatures \( P_{N_2} \) is virtually equal to the total pressure.

Now the temperature coefficient of the solubility in alpha iron is positive, so that the given solubility of 0.0004 % N at 750 °C is certainly an upper limit for the solubility (still at 1 atm) at temperatures lower than 750 °C. For the solubility \( C \) (in weight \% N) at some other pressure we have

\[ C < 0.0004 \sqrt{P_{N_2}} \]  \[ (11) \]

An upper limit of maximum solubility is then immediately found by substituting for \( P_{N_2} \) the dissociation pressure of Fe₄N as calculated from (10). If it is desired to avoid this pressure, which only arises as a secondary quantity, then one may combine directly the formulae (9) and (11) and write

\[ C_{\max} < \frac{0.0004 P_{NH_3}}{\sqrt{K_{NH_3} P_{H_2}}} \]  \[ (12) \]

where \( P_{NH_3} \) and \( P_{H_2} \) are the partial pressures of \( NH_3 \) and \( H_2 \) in the gas mixture of 1 atm at which the maximum solubility is reached and the formation of Fe₄H begins.

Thus we find the values given in column 2 of table III for the upper limit of maximum solubility.

The values of maximum solubility found experimentally by the various research workers do not by

Table III. Values of the upper limit of maximum solubility of nitrogen in alpha iron calculated for various temperatures, and the experimental values of maximum solubility found by various investigations.

<table>
<thead>
<tr>
<th>Temp. (in °C)</th>
<th>Maximum solubility (in weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated (upper limit)</td>
</tr>
<tr>
<td>590</td>
<td>0.040 (0.5 10)</td>
</tr>
<tr>
<td>550</td>
<td>0.035 (0.5 10)</td>
</tr>
<tr>
<td>500</td>
<td>0.030 (0.5 10)</td>
</tr>
<tr>
<td>450</td>
<td>0.025 (0.5 10)</td>
</tr>
<tr>
<td>400</td>
<td>0.020 (0.5 10)</td>
</tr>
<tr>
<td>300</td>
<td>0.010 (0.5 10)</td>
</tr>
<tr>
<td>200</td>
<td>0.005 (0.5 10)</td>
</tr>
<tr>
<td>100</td>
<td>0.002 (0.5 10)</td>
</tr>
<tr>
<td>20</td>
<td>0.0004 (0.5 10)</td>
</tr>
</tbody>
</table>

10) A. Fry, Stahl und Eisen 43, 1271-1279, 1923.
13) W. Köster, Arch. Eisenhüttenwes. 8, 637-658, 1930.
any means agree one with the other, as may be seen from column 3 of this table. Remarkably enough, our calculated values correspond almost completely with Köster’s experimental values \(^{14}\). Even the lowest values taken from literature are therefore probably to be regarded as an upper limit.

**Solubility of nitrogen in liquid iron and absorption of this element when welding with bare electrodes**

In the foregoing we have considered the solubility of nitrogen only in solid iron. In order to judge the maximum amount of nitrogen that might be absorbed during the process of welding we should have to know the solubility of nitrogen in liquid iron. Considering that welding is usually done in air, at a pressure of 1 atm, the partial pressure of nitrogen then being about 0.8 atm, the solubility at 0.8 atm nitrogen pressure is of particular importance to us.

Various investigators have determined the solubility of nitrogen in liquid iron at 1 atm nitrogen pressure. The highest and possibly, the most reliable values were found by Köster \(^{14}\). The solubility \(C_{1\text{atm}}\) at 1 atm as a function of the absolute temperature \(T\) can be represented, according to his measurements, by the formula

\[
\log C_{1\text{atm}} \text{ (in wt. } \% \text{ N)} = \frac{1170}{T} - 0.715. \tag{13}
\]

Substituting for \(T\) the boiling temperature of iron, about 2750 °K, we find a nitrogen content of 0.072 \%. Considering that the nitrogen pressure is only 0.8 atm, this value has to be reduced to 0.072 \% of 0.8 = 0.065 \%. For \(T < 2750 \text{ °K}\) equation (13) would yield still smaller values of solubility.

Now Losana’s measurements (see table I) and also those of other investigators show that when welding with bare electrodes nitrogen may be absorbed in quantities three to four times as much as the maximum quantity (0.065 \%) conformable to equation (13).

In our calculations, however, it has been tacitly assumed that the liquid iron is in contact with nitrogen of the same temperature. In point of fact this is certainly not the case, for all available experimental data indicate that temperatures of at least 6000 °K are reached in the welding arc. At this temperature the concentration of atomic nitrogen in the gas phase is already about \(10^5\) times as great as that at the boiling point of iron \(^{15}\). Taking this into account it is surprising that not a still greater nitrogen content is found when welding with bare electrodes. As we shall see from what follows, in the deposition of the metal more nitrogen is indeed absorbed but this is partly released again in the cooling down and solidifying of the metal.

**Injurious effects of oxygen and nitrogen**

**Porosity**

As already stated, highly porous beads are obtained when welding with bare electrodes. Everywhere in literature we find that this is caused by the formation of CO as a result of the reaction between the oxygen absorbed while welding and the carbon always present in technical iron and steel. Our foregoing considerations led us to presume that this is only half the truth and that also nitrogen is to be regarded as a cause of porosity. In order to investigate this we prepared an iron entirely free of carbon and made plates of it 10 mm thick and rods 4 mm in diameter. With these carbon-free rods were welded on the carbon-free plates and, as was expected, these were found to be almost as porous as the beads obtained when using normal technical wire and plates both containing about 0.1 \% C.

Apart from the formation of CO there is obviously another cause of porosity, and this may be assumed to be the release of part of the dissolved nitrogen.

**Mechanical strength**

The mechanical strength of welds is very often judged by measuring the impact value, i.e. the energy required to break in half in one blow a bar of iron of certain dimensions in which a certain notch has been made. Owing to the great porosity and the high oxygen and nitrogen content (see table I) welds made with bare electrodes have such a low mechanical strength that there is hardly any sense in measuring their impact value. In a subsequent article we shall see that welds made with modern coated electrodes have much lower but still relatively high oxygen and nitrogen contents, the nitrogen content varying from about 0.005 \% to about 0.033 \% according to the type of electrode and the oxygen content from about 0.03 to about 0.12 \%. It appears that a lower nitrogen content is always accompanied by a lower oxygen content and a higher impact value. Since the oxygen and nitrogen contents vary in the same direction it is not possible to determine from tests on welds the effect that each of these elements separately has on the impact value.

We have therefore carried out a number of experiments with iron of the composition of the bare

\(^{14}\) T. Köster, Arch. Eisenhüttenwes. 15, 77-82, 1941.

electrodes, first removing oxygen and nitrogen by repeated high-frequency melting in pure argon and then adding known quantities of one impurity at a time (nitrogen or oxygen) 16). These experiments have shown that up to a content of 0.033 % nitrogen does not affect the impact value, whereas the addition of oxygen up to the aforementioned content of 0.12 % is accompanied by a gradual lowering of the impact value.

Furthermore, the experiments indicate that the great influence of oxygen on the impact value is due to the fact that this element is present in the form of an oxide which is partly contained along the crystal boundaries. Consequently the metal readily breaks between the crystals.

Ageing

Both after rapid cooling and after mechanical working steel is apt to be unstable, gradually increasing in hardness and decreasing in ductility. One then speaks of "ageing", in the former case "quench ageing" and in the latter case "strain ageing". These processes may be accelerated by heating to 100 or 200 °C.

Ageing after mechanical working is particularly of great technical importance as a great deal has been published on this subject. Many investigators attribute this strain ageing to the presence of oxygen, whilst many others ascribe it to the presence of nitrogen. The cause of the controversy lies in the fact that the experiments have been carried out with technical steels containing both oxygen and nitrogen.

By studying this phenomenon with iron and steel, specially made in this laboratory, not containing both these impurities together, it has been possible to arrive at the definite conclusion that nitrogen causes strain ageing whereas oxygen does not.

Apparently this is related to the fact that nitrogen has a certain solubility in alpha iron (a solubility decreasing with temperature), whereas oxygen is practically insoluble in alpha iron (cf. figs. 1 and 3). Consequently supersaturated solutions of nitrogen in alpha iron may easily be obtained, for instance by rapid cooling from P to Q in fig. 3. If there is a great supersaturation there may be a spontaneous precipitation of finely divided Fe₃N (quench ageing). If there is only slight supersaturation (for instance after comparatively slow cooling) then one can imagine that mechanical working is necessary to start precipitation (strain ageing). It is also possible that in the latter case it is not so much a question of precipitation of a new phase as the occurrence of changes in concentration in the homogeneous solution, which have an adverse effect upon ductility.

As table III shows, the solubility of nitrogen in alpha iron at room temperature is at most a few ten-thousandths per cent and therefore even very small quantities of nitrogen may be expected to cause phenomena of ageing. This is borne out by our experiments.

Useful effects of oxygen and nitrogen

Transmission of heat

Wyer 17) has pointed out that heat transfer to the metal is governed to a high degree by dissociation of the gas in the arc, not only when welding in hydrogen but also when welding in air.

Dissociation of the oxygen and nitrogen requires a great deal of energy and consequently the arc voltage is greater than that in a monatomic gas. The atoms recombine for the greater part on the surfaces of the electrodes, thereby releasing again their dissociation energy.

Transfer of the metal

Of fundamental importance is the influence that oxygen in combination with carbon exercises upon the transfer of the metal from the electrode to the workpiece.

At first sight it always appears strange that it should be possible to weld "overhead", the droplets being "shot" upwards against the force of gravity. Various investigators have already pointed out that one of the factors playing a part here is the production of gases during the melting of the metal.

To throw more light upon this question we have carried out some experiments with 4 mm wire made of the carbon-free iron mentioned in the section on "Porosity". Overhead welding was found to be impossible with bare electrodes of this kind. Droplets were formed at the end of the electrode but they ran downward along the rod. The experiments were repeated with the same kind of iron but with 0.1 % C added, when it was indeed found possible to obtain an upward transfer of the metal.

We have already seen (table I) that when welding with bare electrodes the C content drops to very low values as a consequence of the reaction with oxygen. The experiments described above give the impression that this reaction leads to small explosions in the melting metal which act as propelling forces upon the drops.


The experiments described seem to show that any other propelling forces which may act besides the development of CO and which have been summed up by Sack (18) in this journal do not play any important part. These other forces must exercise their influence also when welding with carbon-free rods but they prove to be incapable of overcoming the force of gravity in the transfer of the metal.

Apart from the already mentioned objections attached to welding with bare electrodes, overhead welding with these electrodes, even if they contain carbon, is hardly practicable on account of the fact that owing to the absence of a "cup" much of the metal is thrown off laterally.

If the formation of CO in the metal is indeed the propelling force when welding with bare electrodes, then not only the absence of carbon (even when oxygen is present) but also the absence of oxygen (even when carbon is present) must neutralize the welding action proper. This conclusion is borne out by experiments of Doan and Smith (19). They welded with bare electrodes in different-gas atmospheres. In helium, argon and nitrogen the droplets just fall apparently under the action of gravity. There is no arc blow and no crater is formed (an elliptical depression in the molten or solidified pool underneath the tip of the electrode). Consequently there is little penetration. The addition of only a few per cent of oxygen to the inert gas was sufficient to make the welding normal; the droplets are then driven out with force, a crater is formed and the penetration is normal.

In welding with coated electrodes too the development of gases is fundamental for the transfer of the metal. With the best coated electrodes, however, these gases are not formed by the reaction between oxygen and the carbon in the metal because the coating affords protection against this oxidation. The production of gases then takes place in the coating and, as we shall see in a later article, constitutes one of the most important functions of the coating.

19) G. E. Doan and M. C. Smith, Welding J. 19, 110a-116a, 1940.

The influence of cooling on high-pressure discharges in tubes and in free air is theoretically discussed and—for the case of discharges in tubes—verified experimentally. The agreement between experiment and theory is satisfactory.


To obtain a satisfactory emission from an oxide-coated cathode, the degassing of the tube and the various parts inside it must be carried out in a special order and the correct pumping procedure has to be found for each type of tube. One of the factors influencing the cathode-emission has been made the subject of a special investigation which led to the following conclusions: a) glass heated to 400 °C evolves a small amount of hydrochloric acid; b) in a vacuum tube this HCl reacts with the carbonate or the oxide to give BaCl₂ or SrCl₂; c) when the cathode is subsequently heated these chlorides evaporate and condense on the grid and the anode; d) under electron bombardment the chlorides decompose, thereby producing Cl-atoms or Cl-ions which poison the cathode.


In the quaternary system (Mg, Zn) (W, Mo)O₄ four different crystal structures appear. The fluorescence and absorption of products of these structures are studied.


As shown in a previous paper, the fluorescence of solid solutions of (Zn, Mg)WO₄ can be interpreted simply as the superposition of the fluorescence of its two components; but in the systems (Ca, Pb) WO₄ (Sr, Pb)WO₄ and (Ba, Pb)WO₄ new emission bands were observed which were attributed to tungstate groups with mixed surroundings of lead and calcium, strontium or barium ions. In this paper the systems (Ca, Sr)WO₄, (Ca, Sr)MoO₄, and (Ca, Mg)₃ WO₆ are shown to behave as (Zn, Mg)WO₄, whereas (Ca, Pb)MoO₄ behaves as (Ca, Pb)WO₄.


The potential differences existing across an oxide coating during short-time emission (condenser discharge with an “RC-time” of 10⁻⁴ sec) have been measured.

For this purpose a new measuring method was worked out. Using this method it was found that at current densities of about 5-10 A/cm² remarkable high potential differences exist across the oxide coating (50-200 V) at the normal working temperature (900-1100 °K) at which the experiments were carried out.


The main subject of this article is the reaction between FeO and C. Assuming a mixture of liquid Fe and liquid FeO to possess a Gibbs entropy of mixing and a van Laar heat of mixing, the activity of FeO in liquid Fe is computed and compared with observed solubilities. Next the activity of C in Fe is derived by comparing the composition of CO-CO₂ gas phases in equilibrium with liquid iron and with graphite, using spectroscopic and thermal data. The quotient \( \frac{a_{CO}}{a_{FeO} \cdot a_{C}} \) computed from the activities is a constant only if the C-concentration < 0.1 percent by weight. This is confirmed by independent arguments.


A calculation is given of the input impedance of an antenna consisting of a vertical wire fed against a
system of two or four equal horizontal wires. The latter are placed end to end and symmetrically around the base of the antenna proper. The investigation is based on the assumption of sinusoidal current distribution. For a quarter-wave antenna the radiation resistance is found to be approximately 20 ohms, both for two-wire and for four-wire systems.


A rectangular noise spectrum is applied to a valve with a non-linear current-voltage characteristic. The energy frequency spectrum is computed. It is shown that the partial spectra resulting around multiples of the original central frequency have different forms. They are distinguished by their order. If the characteristic is given in the form of a polynomial or of a power series, a formula is obtained from which all partial spectra can be computed directly. Finally, the presence of one or more carriers is taken into account.


As was described in Part I, certain alloys of Ag, Cu and Ni with a few atomic % of a homogeneously dissolved metal having a sufficient affinity for oxygen can be dispersion-hardened by diffusing O into them. Two conditions must be satisfied. Firstly the oxide must be formed not as a surface layer but dispersed in the interior of the alloy. In this connection the penetration of the reaction front and the oxide concentration was calculated. Secondly the dispersion must be very fine. The greater the affinity for O of the basic metal, the greater must be the affinity of the solute to produce oxide that conglomerates slowly enough. This was worked out in a tentative thermodynamical scheme.

In Part II diffusion coefficients of O in internally oxidized alloys of Ag and Cu are given. X-ray and electrical resistivity measurements support the view that the MgO and Al₂O₃ particles that harden silver are very small. The mechanical properties are not much affected by long annealings at high temperature. Creep and recrystallization are slowed down considerably. A drawback is the intercrystalline brittleness of these materials, which is less serious when somewhat smaller hardness is aimed at. Single crystals are completely ductile. Some peculiar metallographic effects are explained.


A design method is developed for chokes carrying A.C. only, to enable the most economical dimensions to be found for any given electrical characteristics. Formulae and tables are given for rectangular types of chokes with and without limitations on the stacking height. It is also shown briefly how the method may be applied to chokes carrying D.C. with superimposed A.C.


Aluminium can be covered electrolytically with a porous layer of aluminium oxide, and oxidation afterwards in boric acid gives rise to the formation of a crystalline layer. The experiments described below show undoubtedly that this layer only fills up the holes of the amorphous Al₂O₃. Moreover, there is a correlation between the current density in oxalic acid and the porosity of the amorphous layer thus formed.