Chemical reactions and metal flow in welding

Subjects of Interest

- Objectives
- Introduction
- Gas-metal reactions
- Slag-metal reactions
- Fluid flow in arcs
- Fluid flow in weld pools
- Metal evaporation
- Rate of metal transfer
Objectives

• This chapter provides information on chemical reactions occurring during welding. This is for example the reactions between the weld and gases (oxygen, nitrogen and hydrogen) and slag which significantly affect microstructure of the weld, and hence the properties of the weld.

• Students are required to understand the effect of chemical reactions and the fluid flow on the shape of the resultant weld pool.
Introduction

Effects of gases on weld soundness

During welding, nitrogen, oxygen and hydrogen can dissolve in the weld metal, which in turn significantly affect the soundness of the resultant weld.

<table>
<thead>
<tr>
<th>TABLE 3.1 Effect of Nitrogen, Oxygen, and Hydrogen on Weld Soundness</th>
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</thead>
<tbody>
<tr>
<td><strong>Nitrogen</strong></td>
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<tr>
<td>---</td>
</tr>
<tr>
<td>Steels</td>
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<tr>
<td>Austenitic or duplex stainless steels</td>
</tr>
<tr>
<td>Aluminum</td>
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<tr>
<td>Titanium</td>
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</table>
Introduction

Techniques used to protect weld pool

There are various techniques used to protect weld pool during fusion welding, each of which provides different degree of weld metal protection.

<table>
<thead>
<tr>
<th>Protection Technique</th>
<th>Fusion Welding Process</th>
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<td>Gas</td>
<td>Gas tungsten arc, gas metal arc, plasma arc</td>
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<td>Slag</td>
<td>Submerged arc, electroslag</td>
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<td>Gas and slag</td>
<td>Shielded metal arc, flux-cored arc</td>
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<td>Vacuum</td>
<td>Electron beam</td>
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<td>Self-protection</td>
<td>Self-shielded arc</td>
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Oxygen and nitrogen levels expected from several arc welding processes.
Introduction

Weld metal protection in different techniques

**GTAW**
- The cleanest arc welding process due to inert gases used.
- Special gas-filled box can be used.
- Stable arc.

**GMAW**
- Very clean but not as clean as **GTAW** due to unstable arc with consumable electrodes.
- $CO_2$ is sometimes used as shielding gas in which it can decompose to give $O$ at high temperature.

**SMAW**
- Weld pool protection is not effective as in **GTAW** or **GMAW** because the gas flow in not well directed to the weld pool. $\rightarrow$ Higher $O$ and $N$ levels.
- Decomposition of slag is possible $\rightarrow$ increase $O$ level.

**Self-shielded arc welding**
- Used for strong nitride formers such as $Al$, $Ti$, $Zr$.

**SAW**
- Oxygen level varies depending on the composition of the flux. Acidic flux (containing $SiO_2$) gives high $O$ level.
Gas-metal reaction

• The gas-metal reactions take place at the interface between the gas phase and the liquid metal, including the dissolution of nitrogen, oxygen and hydrogen in liquid metal and the evolution of CO.

• In arc welding, portions of $N_2$, $O_2$ and $H_2$ can dissociate (or even ionize) under the high temperature of the arc plasma. These atomic $N$, $O$ and $H$ can dissolve in the molten metals.

$$\frac{1}{2}N_2(g) \rightarrow N$$
$$\frac{1}{2}O_2(g) \rightarrow O$$
$$\frac{1}{2}H_2(g) \rightarrow H$$

Where $N$, $O$, $H$ are dissolved nitrogen, oxygen and hydrogen in liquid metal.

Equilibrium concentration of hydrogen as a function of weld pool location.
Nitrogen

- Copper, Nickel
  \(N_2\) can then be used for shielding gas in welding.
- Fe, Ti, Mn and Cr
  Require protection

- \(N\) source is from the air and sometimes added purposely to the inert shielding.
- \(N\) is an *austenite stabiliser*, \(\Rightarrow\) decreasing the ferrite content.
- \(N\) increases the risk of *solidification cracking*.
- Form *brittle nitrides*, i.e., \(FeN_4\) in a ferrite matrix \(\Rightarrow\) *crack initiation*.

*Effect of nitrogen on the RT mechanical properties of mild steel welds.*

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Tapany Udomphol

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Oxygen

Source  air, excess oxygen in oxyfuel welding, or \( O, CO \) in shielding gas, or decomposition of oxide in flux and from slag-metal arc reaction.

Effect  oxygen can oxidize carbon and other alloying elements, depressing hardenability, producing inclusions. \( \rightarrow \text{Poor mechanical properties.} \)

\[
CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)
\]

\[
CO(g) \rightarrow C(s) + \frac{1}{2}O_2(g)
\]

Ex: in oxyacetylene welding

- Excess oxygen \( \rightarrow \) low carbon level
- Excess acetylene \( \rightarrow \) high carbon level (carburizing flame)

Poor mechanical properties

Solution: use oxygen : acetylene ratio close to 1.

Effect of oxygen equivalent (OE) on ductility of titanium welds.

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Hydrogen in steel welds

Source

- Combustion products in oxyfuel ($O_2+C_2H_2$) welding
- Decomposition products of cellulose-type ($C_6H_{10}O_5)_x$ electrode covering in SMAW.
- Moisture or grease on the surface of the workpiece/electrode.
- Moisture in the flux, electrode covering, shielding gas.

Hydrogen reduction methods

- Avoid hydrogen containing shielding gas, cellulose-type electrode.
- Dry the electrode covering to remove moisture.
- Clean the workpiece and filler wire to remove grease.
- Using $CaF_2$ containing flux or electrode covering.
Hydrogen in aluminium welds

Source

• Oxide films on the surface of the workpiece or electrode can absorb moisture from the air and introduce hydrogen into molten aluminium during welding.
• Low solubility of hydrogen in aluminium at lower temperature → Hydrogen is rejected into the weld pool by the advancing solid-liquid interface. → porosity.

Solutions

• Surface cleaning and thermo-vacuum degassing.
• Adding Freon (CCl₂F₂) to the shielding gas.
• Magnetic stirring to help hydrogen bubbles to escape.
• Keyhole helps eliminate entrapment of oxides and foreign materials in the weld by allowing contaminants to enter the arc stream instead of being trapped in the weld.
Hydrogen in copper welds

Source

- **Hydrogen** can react with **oxygen** to form steam, causing **porosity** in the weld metal.
- **Hydrogen** can also diffuse to **HAZ** to react with oxygen there to form steam along the **grain boundaries**. (micro-fissuring)

Solution

- This problem can be minimized by using **deoxidized copper** for welding.
1) Decomposition of flux

- In the high temperature environment near the arc, it was suggested that all oxides are susceptible to decomposition and produce oxygen.

\[ \text{SiO}_2 \rightarrow \text{SiO}(g) + \frac{1}{2} \text{O}_2(g) \]
\[ \text{MnO} \rightarrow \text{Mn}(g) + \frac{1}{2} \text{O}_2(g) \]

CaO, K_2O, Na_2O, TiO_2, Al_2O_3, MgO, SiO_2, MnO

Oxide stability decreases

Note: CaF_2 reduces the oxidising potential of welding fluxes by acting as a dilutent.

2) Oxidation by oxygen in metal

\[ \text{Mn} + \text{O} \rightarrow \text{MnO} \]
\[ \text{Si} + 2\text{O} \rightarrow \text{SiO}_2 \]
\[ \text{Ti} + 2\text{O} \rightarrow \text{TiO}_2 \]
\[ 2\text{Al} + 3\text{O} \rightarrow \text{Al}_2\text{O}_3 \]

3) Desulphurisation in liquid metal

\[ S + \text{CaO} \rightarrow \text{CaS} + \text{O} \]
Effect of flux on weld metal composition

\( \text{CaF}_2 \) decreases the extent of manganese and oxygen transfer from the flux to the weld metal whereas \( \text{FeO} \) gives the opposite effect.

**CaF\(_2\) addition**

Weld metal oxygen, manganese

**Note:** however, the flux additions also result in losses of alloying elements such as Cr, Mo and Ni.

**Solution**

Adding ferroalloy powder (Fe-50%Si and Fe-80%Mn)

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Types of fluxes

• The use of proper fluxes helps to control weld metal composition as well as to protect the weld from the air.

• Welding fluxes can be divided into three groups based on the type of the main constituents.

A) Halide-type fluxes: \( \text{CaF}_2-\text{NaF}, \text{CaF}_2-\text{BaCl}_2-\text{NaF}, \text{KCl-NaCl-Na}_3\text{AlF}_6 \).

Oxygen free- use for welding titanium, aluminium

B) Halide-oxide type fluxes: \( \text{CaF}_2-\text{CaO-Al}_2\text{O}_3, \text{CaF}_2-\text{CaO-SiO}_2, \text{CaF}_2-\text{CaO-Al}_2\text{O}_3-\text{SiO}_2, \text{CaF}_2-\text{CaO-MgO-Al}_2\text{O}_3 \).

Slightly oxidizing - use for welding high alloy steels

C) Oxide type fluxes: \( \text{MnO-SiO}_2, \text{FeO-MnO-SiO}_2, \text{CaO-TiO}_2-\text{SiO}_2 \).

Mostly oxidizing - use for welding low carbon or low alloy steels
The concept of basicity index (BI) was adopted in steelmaking to explain the ability of the slag to remove sulphur from the molten steel and is also now used to indicate the flux oxidation capability.

\[ BI = \frac{\sum (\% \text{ basic oxide})}{\sum (\% \text{ nonbasic oxide})} \]

\[ BI = \frac{CaF_2 + CaO + MgO + BaO + SrO + Na_2O + K_2O + Li_2O + 0.5(Mn) + FeO}{SiO_2 + 0.5(Al_2O_3 + TiO_2 + ZrO_2)} \]

- Acid: \( BI < 1.0 \)
- Neutral: \( 1.0 < BI < 1.2 \)
- Basic: \( BI < 1.2 \)
Excessive weld metal oxygen

• *Excessive weld metal oxygen* leads to *oxide inclusions* lower weld metal mechanical properties by acting as *fracture initiation sites*.

• *Oxygen* can also react with *carbon* to form CO gas during solidification \( \rightarrow \) *gas porosity*.

• However *basic fluxes* have a high tendency to absorb moisture, resulting in *hydrogen embrittlement*. Sometimes can cause unstable arcs.

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*Fracture initiation at an inclusion in flux-core arc weld of high strength low-alloy steel.*

*Toughness*

*Wormhole porosity in weld metal.*

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**Electrochemical reactions**

**Anodic oxidation reactions**

\[
M(\text{metal}) + nO^{2-}(\text{slag}) \Rightarrow MO_n(\text{slag}) + 2ne^{-}
\]

\[
O^{2-}(\text{slag}) \Rightarrow O(\text{metal}) + 2e^{-}
\]

For electrode positive polarity, these reactions occur at the electrode tip-slag interface or the weld pool-slag interface in the electrode negative polarity.

**Cathodic reduction reactions**

\[
M^{2+}(\text{slag}) + 2e^{-} \Rightarrow M(\text{metal})
\]

\[
Si^{4+}(\text{slag}) + 4e^{-} \Rightarrow Si(\text{metal})
\]

\[
O(\text{metal}) + 2e^{-} \Rightarrow O^{2-}(\text{slag})
\]

For electrode positive polarity, these reactions occur at the weld pool-slag interface or the electrode tip-slag interface in the electrode negative polarity.

**Losses of alloying elements**
**Pickup of oxygen at anode.**

**Reduction of metallic cations from the slag, removal of oxygen from the metal**
Electrochemical reactions

Anode  Oxygen pick-up

Cathode  Oxygen removal

Electrode positive polarity

*Oxygen pickup* at electrode tip-slag interface
*Oxygen removal* at weld pool-slag interface

Electrode negative polarity

*Oxygen pickup* at weld pool-slag interface
*Oxygen removal* at electrode tip-slag interface

*Oxygen contents of the welding wire, melted electrode tips, and detached droplets for both electrode positive and electrode negative polarities.*

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Fluid flow in arcs

The **driving force for the fluid flow** in the arc is the electromagnetic force or **Lorentz force**. (the buoyancy force is negligible)

\[ F = J \times B \]

Where \( J \) is the current density with its vector in the direction of the electric current flows. \( B \) is the magnetic flux vector

**Note:** \( F, J, B \) are perpendicular to each other following the rule of thump.

This Lorentz force affects the **shape of the arc** (depending on the electrode tip geometry) and hence influences in the **shape of the weld pool**.
**Arcs shape**

- The *electric current* tends to be **perpendicular** to the electrode tip surface and the workpiece surface and induces a *magnetic field* (with its direction out of the plane of the paper - front and back views of arrow).

- Both *electric current* and *magnetic field* produce downward and inward forces, which push the ionic gas to **impinge on the workpiece surface** and turn outward along the workpiece surface.

- More of downward movement in the sharp electrode tip, producing a *bell-shaped arc*, and less downward movement in the flat electrode tip, producing a *more constricted arc*.

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![Diagram showing electric current and magnetic field effects on the arcs shape](image)
Velocity and temperature field

- Downward and inward momentums due to electric current and magnetic field cause different fluid flow in sharp and flat electrode tips.

**Note:** Downward momentum is stronger in the sharp electrode tip than in the flat electrode tip.

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Power density and current density distribution

Where

- \( q \) is the power density
- \( Q \) is the power transfer to the workpiece
- \( a \) is the effective radius of the power density distribution
- \( j \) is the current density
- \( I \) is the welding current
- \( b \) is the effective radius of the current density distribution.

\[
q = \frac{3Q}{\pi a^2} \exp \left( - \frac{r^2}{a^2/3} \right)
\]

\[
j = \frac{3I}{\pi b^2} \exp \left( - \frac{r^2}{b^2/3} \right)
\]

Note: Power and current density distributions at the anode (workpiece) flatten and widen as the arc length increases.
Driving forces for fluid flow in the weld pool include:

- **Buoyancy force**
- **Lorentz force**
- **Shear stress induced by surface tension gradient at the weld pool surface.**
- **Shear stress acting on the pool surface by the arc plasma.**
- **Arc pressure (only small influence)**
Driving forces for weld pool convection

**Buoyancy force**
Cooler liquid metal at point \( b \) is heavier than point \( a \) causing gravity sinks along the pool boundary and rises along the pool axis.

**Lorentz force**
Liquid metal moves downward
Electric current and magnetic field cause the liquid metal flows downward along the weld pool axis and rises along the weld pool boundary.

**Surface tension force**
Warmer liquid metal having a lower surface tension \( \gamma \) at point \( b \) pulls out the liquid metal in the middle (point \( a \)) along the pool surface.

**Arc shear stress**
High speed outward movement of plasma arc lead to outward shear stress, hence, causing metal flowing from the centre to the edge of the pool.
Weld penetration improvement

Weld pool depth (weld penetration) can be increased by

- Increasing Lorentz force
- Using surface active agent (altering surface tension)
- Reducing arc length (forced convection driven by plasma jet – altering plasma shear stress)
- Reducing turbulence flow
- Using active flux
Weld penetration improvement

- **Increasing Lorentz force**

  - The **Lorentz force** makes the weld pool much deeper as compared to the **buoyancy force**.
  
  - The liquid metal pushed downward by the **Lorentz force** carries heat from the heat source (at the middle top surface) to the pool bottom and causes a **deep penetration**.

(a) Weld produced by buoyancy force, (b) by Lorentz force.
Weld penetration improvement

- Using surface active agent

Small amounts of surface active agents reverse Marangoni convection and make the pool much deeper.

EX: S, O, Se, and Te used in welding steels and stainless steels.

YAG laser 304 stainless steel welds (a) 40 ppm and (b) 140 ppm sulphur.
Reversing Marangoni convection

The direction of the flow changes from **outward** to **inward** on the surface due to the **addition of surface active agent**.

A reverse Marangoni convection makes the weld pool deeper.
Weld depth improvement by sulphur addition in steel

20 ppm sulphur

Outward surface flow carries heat from the heat source to the pool edge and results in a shallow and wide pool.

150 ppm sulphur

Inward surface flow turns downward to deliver heat to the pool bottom and result in a much deeper pool.

Convection stationary laser weld pools of steels with (a) 20 ppm sulphur and (b) 150 ppm sulphur.
Weld pool depth improvement

- Reducing arc length (forced convection driven by plasma jet)

**Long arc length** outweighs both Lorentz force and the surface tension.

Arc length VS voltage and heat

Stationary gas-tungsten arc weld in a mild steel made with a 2-mm and 8-mm arc length.
Weld penetration improvement

- Reducing turbulence flow

Turbulence flow increases effective viscosity and convection slows down.

Weld pool shapes and isotherms in a 304 stainless steel with 50 ppm sulphur (a) laminar flow, (b) turbulence flow.
Weld pool depth improvement

- **Using active flux**
  - *Active flux* in *GTAW* has been found to dramatically increase weld penetration in steels and stainless steels.
  - Using *fluxes* consisting of *oxides* and *halides* and mixed with *acetone* to form a paste and painted as a thin coating other the area to be welded.
  - *Deeper penetration* is caused by *arc constriction* and the vapourised flux constricts the arc by capturing *electrons* in the cooler outer region of the arc.

Gas tungsten arc welds of 6-mm thick 316L stainless steel
(a) without a flux (b) with a flux.
Metal evaporation

• **Loss of alloying elements**

High welding temperature causes *evaporation of metals* in the weld pool especially *alloying elements* affecting mechanical properties.

Ex: Mg loss in aluminium weld results in a substantial reduction of tensile properties due to decreased solid solution strengthening of lower amount of Mg.

**Vapour pressure**

**Tendency to evaporate**
Metal evaporation

• Explosion of metal droplets

*High arc temperature* during welding can also cause *evaporation of metal droplets* when transfer from the filler wire to the weld pool through the arc.

*Mg* and *Zn* have high vapour pressure → high tendency for explosion of metal droplets

Spattering
Metal transfer

**Modes of metal transfer**

1) **Short circuit transfer**
2) **Globular transfer**
3) **Spray transfer**
4) **Rotary spray transfer**

- **Spatter** (normally found in globular transfer) can be solved by using proper shielding gas, current or pulse arc transfer.
Effect of shielding gases on metal transfer

- \( \text{CO}_2 \) and \( \text{N}_2 \) normally give globular transfer, greater instability in the arc and chemical reaction between the gas and superheated metal droplets → considerable spatters. This can be changed to spray transfer by treatment of the wire surface.

- **EX:** In GMAW globular spray is typical when using \( \text{CO}_2 \) as the shielding gas (no matter how high the current used) → spatter. Solutions: using (20-25%) \( \text{Ar} \) and ~80-75% \( \text{He} \).

- Mixtures of \( \text{Ar} \) and \( \text{He} \) are used in welding *non-ferrous* (especially \( \text{Al}, \text{Cu} \)).

- Higher percentage of \( \text{He} \) in the mixture is used for welding thick sections due to higher temperature of the plasma obtained.

\[
\begin{align*}
\text{Ar} & : \text{Ionisation potential} = 15.8 \text{ volt} \\
\text{Plasma temperature} & = 15.8 \times 1000 \text{ K} \\

\text{He} & : \text{Ionisation potential} = 24.6 \text{ volt} \\
\text{Plasma temperature} & = 24.6 \times 1000 \text{ K}
\end{align*}
\]
The volume of metal deposited per unit time can be determined by

\[ V_d = A_d \times v_d \]

Where
- \( V_d \) is the volume of metal deposited per unit time
- \( A_d \) is deposited metal cross section (filler)
- \( v_d \) is welding process travel speed.

The volume of wire electrode per unit time can be determined by

\[ V_w = A_w \times v_w \]

Where
- \( V_w \) is the volume of the electrode wire per unit time
- \( A_w \) is cross section area of the electrode wire
- \( v_w \) is wire linear feed rate.
Total cross section area of melted metal

\[
Nugget \ Area = A_d + A_b = \text{const.} \times \frac{I^{1.55}}{v^{0.903}}
\]

Const. = 1.12 x 10^{-4} for \( I \) = Amp

\( v \) (speed) = in/min

\( \text{nugget area} \) = in²

Const. = 3.33 x 10^{-2} for \( I \) = Amp

\( v \) (speed) = mm/sec

\( \text{nugget area} \) = mm²

If the current and welding speed are known, the nugget area can be estimated.

The nugget area is inversely related to the cooling rate, giving a good indicator of metallurgical structure.
The weld penetration can be predicted through the expression (Jackson definition) below

\[ P = k \times 3 \sqrt[3]{\frac{I^4}{v \times E^2}} \]

Where

- \( P \) is weld penetration (in)
- \( I \) is current
- \( v \) is travel speed (in/min)
- \( E \) is arc voltage (volts)
- \( k \) is a constant between 0.0010-0.0019 depending on the process. (obtained from experiment)
References


• Lecture notes.