WELDING METALLURGY

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Summary

The main metallurgical processes occurring during welding are presented: oxidation and reduction, desulfurization and dephosphorization of liquid metal, supplying of alloying components to weld dissolution and liberation of gases in liquid metal, crystallization, release of non-metallic inclusions and formation of cracks. The decisive effect of these processes on properties of the weld is discussed.

1. Variety of Metallurgical Welding Processes

Joining two metal elements by means of welding consists in the formation of a weld between these two elements. The weld is composed of molten, mixed and, eventually, solidified metal of the edges of welded elements as well as of filler metal (consumable). In principle, melting of metal during welding as well as its chemical and physical reacting with enclosing shield and slag followed by solidification and crystallization reflects melting of steel in a metallurgical furnace and its casting. However, being to some extent similar, welding significantly differs from the aforementioned processes by being very fast and requiring very limited volume of ingredients. The space in which metallurgical processes take place (Figure 1) comprises fusing charge in the form of wire (1) and coating (2) or, alternatively, flux or core of powder-core electrode, liquid metal of the partially molten base (4), liquid and crystallizing part of weld (5) and the area between the electrode and welded element filled with arc plasma, gases and metal vapors (3). The distance between the end of fusing electrode and welded element amounts to several millimeters.

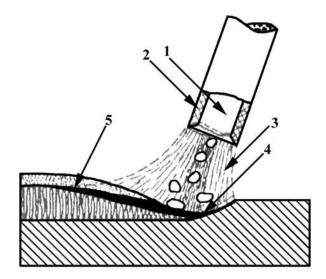


Figure 1. Space between electrode end and welded element in which metallurgical welding processes take place

The butt surface of the wire is an area of numerous reactions proceeding between melting metal and fusing coating. In the arc space it is possible to observe drops of liquid metal moving from the end of fusing electrode towards the welded element. On the surface of the welded element the aforesaid metal drops react with slag and gases filling the arc space. At the same time, alloying components of the coating enter the weld pool. Very high temperature and considerable difference in concentration of individual components as well as a significant area of the contact trigger very intense and dynamic reactions (far from equilibrium).

Metallurgical processes occurring during welding and having a decisive effect on properties of the weld (or padding weld – in case of padding) include:

- oxidation and reduction,
- desulfurization and dephosphorization of liquid metal,
- supplying of alloying components to weld
- dissolution and liberation of gases in liquid metal,
- crystallization,
- release of non-metallic inclusions and formation of cracks.

2. Oxidation and Reduction

Welding is connected with oxidation and reduction reactions resulting in impoverishment or enrichment of liquid metal in elements revealing variable mutual affinity with oxygen, depending on momentary conditions. Not being an alloying component in metal alloys, oxygen forms oxides with metals e.g.: FeO, Fe_2O_3 , Fe_3O_4 (FeO [·] Fe_2O_3). Although approximately 0.2% of oxygen may dissolve in liquid steel, oxygen content in steel should not exceed 0.01-0.02%. Oxygen takes part in most metallurgical processes.

The direction of reaction is influenced, first of all, by temperature and concentration of individual components taking part in the reaction.

Oxidation and reduction proceed according to the following equations:

$$m\mathrm{Me} + \frac{n}{2}\mathrm{O}_2 \Leftrightarrow \mathrm{Me}_m\mathrm{O}_n \tag{1}$$

$$mMe_1O+nMe_2 \Leftrightarrow Me_{2n}O_m+mMe_1$$
 (2)

in the system metal - slag - arc atmosphere. In its initial state, each of these phases may remain in a different relation to the remaining two phases.

The state of equilibrium (1) and (2) is defined by equilibrium constants:

- for Eq. (1)

$$K_{p} = \frac{Me^{m} \cdot O_{2}^{\frac{n}{2}}}{Me_{m}O_{n}}$$
(3)
- for Eq. (2)

$$K_{p} = \frac{(Me_{1} \cdot O)^{m} \cdot Me_{2}^{n}}{Me_{2n}O_{m} \cdot Me_{1}^{m}}$$
(4)

The partial pressure of oxygen in the arc atmosphere may change within a wide range depending on welding technology as well as chemical composition and sort as well as number of gas generating components contained in coating or flux. The concentration of oxygen in slag may also change within a wide range depending on the chemical composition of coating or flux. In slags obtained from coatings e.g. acid-ore based, the said concentration is the highest, which results not only in burning of alloying elements in the weld but also saturating the weld with FeO dissolved therein. High concentration of a given element in metal favors oxidation and transfer of its oxide to the slag. In turn, low concentration favors the reduction of its oxide in the slag and enriches liquid metal in this element.

Reactions of oxidation according to Eq. (1) proceed with various intensity measured by the value of free energy ΔF for a given reaction proceeding at constant volume or the value of thermodynamic potential ΔG for a given reaction proceeding at constant pressure.

Equilibrium constant K_p , free energy ΔF and temperature *T* remain in a strict relationship expressed by the heat of reaction ΔH and change of system entropy ΔS :

$$\log K_{\rm p} = -\frac{\Delta H}{4,575T} + \frac{\Delta S}{4,575}$$
(5)

The dependence of equilibrium constant K_p (equivalent to oxide dissociation pressure) on temperature is illustrated by the curves in Figure 2. The elements which oxidize most intensively at a given temperature T are those whose dissociation pressure P_{O_2} is the lowest.

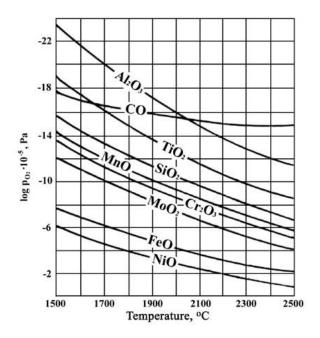


Figure 2. Temperature-dependent dissociation pressure of oxides

Considering related top the processes of oxidation and reduction in metallurgical processes is complicated as these reactions proceed in two phases (slag – metal) and are accompanied by more reactions occurring at the same time e.g. oxidation of manganese, silicon and carbon. Thus, oxygen taking part in the aforesaid reactions is proportionally distributed not only between two phases i.e. slag – metal but also among other individual reactions.

The impact on the course of reaction resulting from the distribution between the two phases should be additionally allowed for in the form of distribution coefficient:

$$\frac{[MeO]}{(MeO)}$$
(6)

with [MeO] denoting oxide concentration in metal, and (MeO) denoting oxide concentration in slag.

The value of coefficient for a given temperature is a constant quantity. In principle, individual reactions require that factor of molar activity $f_{\rm M}$ be taken into consideration. Activity α of a given component M is expressed as:

 $\alpha_{\rm M} = [{\rm M}] f_{\rm M}$

(7)

In general, in order to simplify deliberations and calculations, the activity factor is usually omitted and concentration values are used directly.

The graph presented in Figure 2 refers to the state of equilibrium which establishes in reaction conditions. In fact, in welding conditions such a state will not be reached within the whole range of proceeding reactions. Forecasting the course of reaction according to the graph is, however, confirmed in practice.

Having taken the form of minute droplets and vapors, the metal melting on the end of the electrode enters the surface of metal bath pool through the arc space. At a high temperature the elements building up metal material undergo oxidation, which is additionally favored by a large area of the contact between the droplets and arc atmosphere. In conditions accompanying e.g. welding with bare wire in air atmosphere or in case of CO_2 MIG welding, a weld obtained in this way will have a high FeO content impairing its plastic properties. If a wire with sufficient amount of Mn and Si is used in the process (e.g. in case of CO_2 MIG welding), these elements will undergo partial oxidation in the arc atmosphere, yet their sufficient amount will enter the weld and deoxidize it before the weld solidifies. A similar effect may be obtained during welding with a covered electrode or while welding with a bare wire under flux by supplying enough SiO₂ and MnO to the coating or flux. As a result, SiO₂ and MnO become reduced in the arc, whereas Mn and Si enter the metal bath.

3. Desulfurization of Liquid Metal

Sulfur is one of the elements which cause numerous problems and difficulties during welding processes as it is known for its adverse effect on plastic properties of steels and welds. In conjunction with iron, sulfur forms sulfide FeS characterized by high liquation tendency, whereas if combined with oxide FeO, it forms low-melting eutectic accumulating among solidifying dendrites and being the basic reason for hot cracks. Due to the foregoing, every possible effort is made to reduce sulfur content in steels and welds.

Sulfur enters the weld from a welded material, electrode wire and flux or coating. The distribution of sulfur between liquid metal and slag depends on chemical composition and welding parameters. The selection of components (based on their purity) for production of fluxes and coatings as well as the choice of electrode wire (based on sulfur content) may radically reduce negative impact of sulfur on weld quality. If the general content of sulfur in the flux does not exceed 0.15% and MnO content in the flux is up to 30%, sulfur does not pass from the slag into the weld during a welding process. If, however, sulfur content in the flux exceeds 0.15%, even with MnO content in the flux exceeding 30% it will not be possible to prevent sulfur from passing into metal bath.

Iron sulfide FeS, soluble in iron and slag, is distributed according to distribution law proportionally between these two phases:

$$[FeS] \Leftrightarrow (FeS) \tag{8}$$

MnO excess in slag causes binding of sulfur according to the following reaction:

$$(FeS)+(MnO) \Leftrightarrow (MnS)+(FeO)$$
(9)

Thus, due to the binding of sulfur into insoluble compound MnS, on the border metal - slag FeS may continue to pass into the slag according to Eq. (8).

Applying slags with high MnO content in welding processes is highly recommendable as such slags enable binding of sulfur into manganese sulfide MnS and reduce sulfur content in the weld.

Also the reaction of binding sulfur with calcium finds application in welding processes:

(10)

$$CaO+FeS \Leftrightarrow FeO+CaS$$

However, providing the flux with CaO instead of MnO proves inconvenient as it not only fails to reduce sulfur content in the weld, but, quite the reverse, may increase the aforesaid content. Similar result follows increasing slag acidity by increasing SiO₂ content. Desulfurization with CaO is possible while applying basic slags.

The process of weld desulfurization is effective if manganese content in the metal bath is high enough. The concentration of sulfur in steel is inversely proportional to the concentration of manganese in steel and manganese oxide and calcium oxide in slag and directly proportional to the concentration of manganese sulfide and iron oxide in slag:

$$[S] \cong \frac{(MnS)(FeO)}{[Mn](MnO)(CaO)}$$
(11)

4. Dephosphorization of Liquid Metal

Phosphorus, similarly to sulfur, is an element causing numerous problems in welding processes. In steel phosphorus is usually present as phosphides Fe₂P and Fe₃P causing cold brittleness and increasing the risk of cold crack formation.

In liquid steel phosphorus is usually present as the solution of P atoms (nonphosphides). The elimination of phosphorus consists in its oxidation with iron oxide followed by passing phosphorus oxide into the slag:

$$2P+5FeO = P_2O_5 + 5Fe \tag{12}$$

and

$$3CaO + P_2O_5 = 3CaO \cdot P_2O_5$$
⁽¹³⁾

or

$$4\text{CaO} + P_2\text{O}_5 = 4\text{CaO} \cdot P_2\text{O}_5 \tag{14}$$

Phosphorus content in steel may be reduced by applying basic slag containing some FeO necessary for, first of all, phosphorus oxidation. The content of phosphorus in steel is inversely proportional to the concentration of CaO in the slag and that of FeO in steel and directly proportional to P_2O_5 concentration in the slag:

$$[P] \cong \frac{(P_2O_5)}{(CaO)[FeO]}$$
(15)

In case of low CaO content, P_2O_5 present in the slag may be reduced by carbon again; this will be followed by an increase in phosphorus content in steel. Also in case of welding steel with basic slags, part of phosphorus may pass from the slag into the weld.

Phosphorus found in the weld may come from the electrode wire, parent metal, flux or coating. Manganese ores tend to contain more phosphorus and due to that fact not all of them prove useful for production of coatings and welding fluxes. If manganese flux (~ 40% MnO and ~ 40% SiO₂) contains 0.15% P, welding under flux causes 0.015% P to enter the weld.

If the electrode wire and parent metal contain of maximum of 0.05% P, enriching the weld up to 0.065% P proves risky. For this reason, the content of phosphorus in the flux is reduced to 0.12%. In case of multilayer welding, phosphorus content in the weld increases in each successive layer and in the last layers may reach the similar level as that in the slag. Similarly to other elements, passing of phosphorus into the weld increases with increasing voltage and decreasing intensity of welding current.

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Biographical Sketch

Jan Pilarczyk has received his diploma of Master of Science in Mechanical Engineering from the Silesian Technical University in Gliwice, Poland in 1963, After completing further studies at ESSA Paris. France he obtained a Post-Graduate Welding Engineer Diploma in 1967. In 1972-1973 he served an apprenticeship in Cranfield Institute of Technology, UK. He joined the Instytut Spawalnictwa (The Welding Institute) in Gliwice, Poland in 1963 as a junior research worker in investigations into weldability of steel and mechanical testing of welded structures. He was continuing as a senior research worker and the head of Weldability Department. In 1980-1990 he was the Director for Research, Management and co-ordination of research activities of the Institytut Spawalnictwa, management of State research programs on the area of welding. Since 1991 to date he is being the Director of the Instytut Spawalnictwa. During his association with the Instytut Spawalnictwa he earned a PhD-degree and DScdegree from the Technical University Gliwice, Poland in 1972 and 1977 respectively. In 1991 he was awarded the Professor title by the President of Poland. In 1992 he obtained the European Welding Engineer degree from the ESSA Paris France. His scientific contributions and technical papers (more than 100) have been published in different Technical Journals and Magazines in the field of weldability of steels, case studies, welding development etc. On the other side he is the author of 4 technical books in welding. He is the member or fellow of many scientific, technical and social organizations. In some of them he is a chairman or president.