To a question interaction of metal with complex gases containing oxygen during manual arc surfacing

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ABSTRACT: This article provides a study of the interaction of molten metal with complex gases containing oxygen during manual arc surfacing of low-carbon and low-alloy steels

KEYWORDS: arc welding, flux, low alloy steel, slag, oxide

I. INTRODUCTION

Without protection, the molten metal during surfacing intensively absorbs oxygen and nitrogen from the air, therefore the deposited metal is characterized by low mechanical properties [1].

During the surfacing process, various means of protection are used to isolate the metal from air: electrode coatings, fluxes, protective gases, and vacuum. However, it is usually not possible to completely isolate the metal from the air. Even when surfacing in a vacuum in the chamber, the partial pressure of nitrogen and oxygen may be sufficient to interact with the metal [1,2].

Protective equipment is usually capable of interacting with metal itself. Including inert gases (argon, helium), which may contain a certain amount of nitrogen, oxygen and hydrogen (moisture) and, under appropriate conditions, cause reactions between the metal and the gas [2].

During surfacing, the occurrence of reactions leads to a change in the composition of the melted (usually high-quality) metal and, therefore, to a change in its properties. As a result of reactions, the formation of pores of non-metallic inclusions and other defects in the deposited weld metal is also possible. In this regard, during surfacing, knowledge of the patterns of metallurgical reactions is important, allowing one to predict the composition and, ultimately, the properties of the deposited metal [2,3].

II. LITERATURE SURVEY

There are two main stages of interaction of molten metal with slag and gases: drops of metal formed at the end of the electrode. Depending on the conditions of temperature, interaction time, interfacial surface, equilibrium and initial concentrations at these stages, the direction and completeness of the reactions may be different. [3]

At the bath stage, the oxidation of manganese and carbon increases with increasing its content in the wire, because, despite the high rate of carbon oxidation in droplets, in this case its content in the metal entering the bath turns out to be

much greater. There is also more manganese, the oxidation of which in droplets is inhibited by the combustion of carbon. In the bath stage, the system is further from equilibrium because the initial concentrations are greater and both reactions proceed at a greater rate and completeness. The role of the bath stage also increases significantly with a decrease in the oxidizing ability of the coating, due to the fact that oxidative reactions at the drop stage proceed sluggishly and metal with a high content of manganese and carbon enters the bath, and when welding with a coating containing manganese ore, at the bath stage There is even a reduction of part of the manganese oxidized on the electrode [1,2].

Therefore, reactions at the bath stage have to be taken into account to a greater extent, the less oxidizing conditions the surfacing process is carried out [2,3].

In addition to reactions at the drop and bath stages, in the case of electrode coatings, one must also take into account the chemical reactions that occur between the components of the coatings during their manufacture and heating during the surfacing process (before they melt). The oxidation reactions of metal additives introduced into the coating mixture are of greatest importance. [4]

III. METODOLOGY

Carbon dioxide is an energetic oxidizing agent, interacting with the metal according to the reaction:

$$mCO_2 + nMe \leftrightarrow mCO + Me_nO_m \tag{1}$$

In addition to air and protective gases, sources of oxygen and hydrogen are coatings, which almost always contain various oxides, carbonates and other compounds capable of transferring oxygen to the metal, as well as hygroscopic and bound moisture included in the structure of minerals in the form of molecules in crystalline hydrates or in water the hydroxyl group OH in hydroxides. Hygroscopic and crystallization water can be relatively easily removed and, accordingly, the moisture content in the coating and hydrogen in the weld metal can be reduced by heating the electrode before surfacing to a relatively low temperature.

One of the sources of gas release is surface pollution. These are primarily surface oxides, which, dissolving in the metal during its melting and interacting with it, contribute to the saturation of the bath with oxygen. Surface oxides can also be suppliers of hydrogen. An example is rust, which is a hydrate of iron oxide that decomposes when heated to release water vapor. The moisture absorbed by the oxide film is retained on the surface when heated to a high temperature, as a result of which the absorption of hydrogen by the metal is possible due to the direct interaction of the melt with the moisture entering the bath along with the particles of the oxide film. In addition to the oxide film and adsorbed moisture, the metal surface contains grease and dust contaminants, including organic and sooty substances. Thermal decomposition of organic substances leads to the formation of hydrogen-containing gases, and soot substances can be a source of CO.

The base and filler metal can be contaminated with gases, which, when melted, can pass into the weld metal or be released in the form of gas bubbles, causing porosity.

When the molten metal comes into contact with the oxygen of the gas or slag phase, the oxygen dissolves in the metal, and when the saturation concentration is reached, a separate oxide phase is formed.

At the same time, oxidation of impurities and alloying elements contained in the metal occurs.

Elements with a high affinity for oxygen are oxidized first. The affinity for oxygen can be judged by the value of the standard change in free energy ΔG^0 of oxide formation or by the elasticity of its dissociation p_{O_2}. When a pure substance interacts with oxygen:

$$Me + 1/2O_2 = MeO \tag{2}$$

$$K = \frac{1}{p_{O_2}} \tag{3}$$

$$\Delta G^0 = -RT \ln K = RT \ln p_{O_2} \tag{4}$$

that is, the elasticity of dissociation depends only on temperature, like the equilibrium constant.

However, when interacting with oxygen of the same substance in solution

$$[Me]_{so\,lub} + 1/2O_2 = [MeO]_{so\,lub} \tag{5}$$

it is necessary to take into account the activity of substances

$$K = \frac{a_{MeO}}{a_{Me}p_{O_2}} ; \tag{6}$$

$$p_{O_2} = \frac{1}{K}\frac{a_{MeO}}{a_{Me}} ; \tag{7}$$

that is, in this case, the elasticity of dissociation will depend not only on temperature, but also on the concentration of dissolved substances, since activities change with concentration.

If the partial pressure of oxygen p_{O_2} in the atmosphere above the melt is greater than the pressure (elasticity) of dissociation of the oxide of a given element P_{O_2}, then the atmosphere will be oxidizing in relation to it (oxide formation will occur), and vice versa, if $p_{O_2} < P_{O_2}$, then the atmosphere will be reducing in nature .

Oxidation products are removed into the slag, but may partially become stuck in the metal as it solidifies. When the metal is cooled and especially during its crystallization, secondary reactions of oxide formation are possible due to changes in equilibrium conditions (decreased oxygen solubility). Such oxides mostly remain in the metal in the form of non-metallic inclusions or gas bubbles as a result of the reaction:

$$[C] + [O] = CO \tag{8}$$

Metal oxidation is one of the characteristic processes occurring during manual arc surfacing. Sources of metal oxidation are:

a) oxides present on the molten edges of the base and electrode metal;
b) oxides present in the slag and dissolving in the metal;
c) chemically active slags that release oxygen to the metal as a result of exchange redox reactions;
d) gaseous free oxygen - the presence of complex oxygen-containing gases (carbon dioxide and water vapor), capable of releasing oxygen during decomposition.

During surfacing, the oxidation process of different metals is different. Some metals (Fe, Cu, Ni, Ti) have the ability to dissolve a certain amount of oxygen. Moreover, the solubility of oxygen increases with increasing temperature, and is significantly higher in the liquid phase than in the solid phase.

Oxidation of a metal with gaseous free oxygen occurs according to the following reaction:

$$nMe + O_2 = mMe_{n/m}O_{2/m} \tag{9}.$$

During surfacing, oxidation of the alloy base and impurities occurs, the degree and probability of oxidation of which depends on temperature conditions and concentrations of impurities in the solution and is determined by their affinity for oxygen.

If the metal and oxide are condensed solid or liquid phases, the constant of a given oxidation reaction is determined by the partial pressure of oxygen P_{O_2}, corresponding at a given temperature and pressure to the elasticity of oxide dissociation.

Under specific external conditions under surfacing conditions at different temperatures, the possibility of oxidation or reduction of any oxide as a result of its interaction with a gas phase containing free oxygen is determined by comparing P_{O_2} and the partial pressure of free oxygen in the gas phase, which we denote { P_{O_2} }.

If the pressure { P_{O_2} } is greater than the elasticity of oxide dissociation P_{O_2}, then oxidation will occur; at { P_{O_2} }< P_{O_2} - recovery. When { P_{O_2} }= P_{O_2} neither oxidation nor reduction occurs, which corresponds to equilibrium conditions. This case is not typical for surfacing as a final state. The elasticity of dissociation of oxides in solution p_{O_2}' differs from the elasticity of dissociation of free oxides P_{O_2}. In this case $p_{O_2}' = p_{O_2} a_{ok}^m$, where a_{ok}^m is the degree of saturation of the metal solution with oxide [22].

In air containing oxygen over 20%, the latter is a strong oxidizing agent for iron under conditions of plaka ({ P_{O_2} }> P_{O_2}).

Equilibrium pressure P_{O_2} decreases as oxygen in the solution decreases and it is retained more strongly by the metal.

If a metal is diluted with another metal solvent (Mn dissolved in Fe), that is, its concentration is less than unity, and the oxide is also in solution, then the dissociation elasticity P_{O_2} of such an oxide is:

$$p_{O_2}^{''} = p_{O_2} \frac{a_{ox}^m}{a_{Me}^n} \left(\frac{M_{Me}}{M_{so\,lub}} \right)^n \tag{10}$$

where a_{Me} is the degree of saturation of the solvent with the metal;

M_{Me} and M_{solub} are the molecular weights of the metal and solvent [22].

With a decrease in a_{Me}, the elasticity of oxide dissociation $p_{O_2}^{''}$ increases significantly, therefore, in a solvent it is almost impossible to completely oxidize such a metal additive.

In the melting zone, the oxidation of the metal by surface oxides is carried out by remelting the oxides located on the surface of the electrode metal and on the edges of the products being welded. The degree of metal oxidation by surface oxides increases the long-term storage of some types of electrodes with coatings, the lack of preliminary cleaning of the welded product and electrode wire.

Occurring in connection with the redistribution of oxides between the slag and metal oxidation by oxides dissolving in the metal and located in the slag. Under certain conditions, such a free oxide will tend to distribute between the metal and slag phases, determined by the distribution constant $L_{MeO} = \frac{(MeO)}{[MeO]}$, which changes with temperature, where (MeO) and $[MeO]$ are the concentrations of these oxides in the slag and metal, respectively.

For FeO, this distribution constant depends on temperature $\lg \frac{1}{L_{MeO}} = \lg \frac{[MeO]}{(MeO)} = -\frac{6300}{T} + 1{,}386$; from T_{mel} to 2500° C increases from 0.011 to 0.125 [24].

The oxidation that occurs in connection with exchange reactions with slags that are chemically active in oxygen is described by the equation:

$$Me_x^{''}O_y + yMe^{'} = yMe^{'}O + xMe^{''} \tag{11}$$

Carbonates are used as gas-forming components in the form of marble, dolomite, and chalk. When heated, carbonates decompose according to the following scheme:

$$CaCO_3 = CaO + CO_2. \tag{12}$$

At high temperatures, carbon dioxide dissociates according to the following scheme:

$$2CO_2 = 2CO + O_2 \tag{13}$$

The above reaction constant is determined by the equation:

$$\lg K_{(CO_2)} = \lg \frac{p_{CO}^2 p_{O_2}}{p_{CO_2}^2} = -\frac{29072}{T} + 8{,}81 \tag{14}$$

The partial pressure of free oxygen as a result of dissociation CO_2 at 3000º K is approximately the same as the partial pressure of oxygen in air. Therefore CO_2 is an oxidizing agent for a number of metals, including liquid iron:

$$CO_2 + Fe_ж = [FeO] + CO \tag{15}$$

If CO_2 is present in the gas phase, it is necessary to deoxidize the oxidized metal or take measures to protect the metal from oxidation during welding. In this regard, the use of carbon dioxide can provide protection from air N_2, but does not exclude oxidation. In this regard, to deoxidize the metal, deoxidizers are usually introduced into the electrode wire in the required amount, usually Si and Mn, at a certain ratio between them.

IV.CONCLUSION

The selection of deoxidizers during arc surfacing makes it possible to deoxidize the liquid metal to the required extent and obtain deoxidized weld metal, despite the short duration of metal processing under surfacing conditions and the unattainability of equilibrium in the interaction of the metal with the environment during temperature reduction and crystallization.

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