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Investigation of the interaction of molten metal with nitrogen and hydrogen in the development of the composition of ceramic fluxes for automatic arc welding of low-carbon and low-alloy steels

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ABSTRACT: This article provides a study of the interaction of molten metal with nitrogen and hydrogen in the development of the composition of ceramic fluxes for automatic arc welding of low-carbon and low-alloy steels.

KEY WORDS: automatic arc welding, flux, low alloy steel, hydrogen, nitrogen

I. INTRODUCTION

Nitrides are compounds of metals and other elements directly with nitrogen. Nitrogen, which makes up the bulk of the air, always to some extent participates in the processes of fusion welding of metals, and since its presence is easily determined by methods of analytical chemistry and spectral analysis, the nitrogen content in the deposited metal can be judged on the degree of protection of the welding zone from the surrounding air atmosphere.

Hydrogen forms interstitial solutions with metals in liquid and solid states. With some metals, hydrogen can enter into hydride compounds.

The greatest change in solubility occurs during the crystallization of the metal, therefore, hydrogen, which was dissolved in the liquid metal, should be released and leave the weld pool. Under unfavourable welding conditions and thermophysical properties of the metal, this evolving hydrogen can form pores and discontinuities in the metal. The probability of pore formation will be the greater, the greater the difference in solubility in the liquid and solid states.

The change in the solubility of hydrogen in metals at the melting or crystallization temperature, referred to the solubility of hydrogen in the solid state, can characterize the tendency of the metal to pore formation.

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II. LITERATURE SURVEY

Forms numerous compounds with nitrogen of the d-metal family. d-metals that do not have paired electrons at the d sublevel give very stable compounds with a high melting point and high hardness. Metals such as iron, cobalt, nickel form unstable nitrides that decompose at high temperatures, but also have increased hardness in the crystalline state. [1]
The formation of iron nitrides during welding of low-carbon structural steels leads to the precipitation of crystals Fe_3N (melting point 900 K) during crystallization or during the decomposition of solid solutions. As a result, the weld metal loses its ductility, and the welded joint becomes prone to hot and cold cracking. [2]
Hydrogen forms interstitial solutions with metals in liquid and solid states. With some metals, hydrogen can enter into hydride compounds. [3]
The hydrogen dissolution process consists of separate stages [4]:
1. Dissociation of hydrogen molecules into separate atoms ($\Delta H > 0$).
2. Sorption of hydrogen atoms and the formation of a solution.
3. Formation of hydrides with some metals ($\Delta H < 0$).
For metals that do not form hydrides, the solubility of hydrogen will be determined by the first two stages; requiring significant energy consumption for their development. The general theory of hydrogen embrittlement, sufficiently substantiated, does not yet exist, because hydrogen in solid metals has not been detected by any of the known experimental methods. [5]
Hydrogen in welded joints, due to its high mobility under the conditions of the welding cycle, is distributed unevenly, and at an average permissible hydrogen concentration, local concentrations can be created (fusion line for metals that do not form hydrides, or a heat-affected zone for hydride-forming metals), which cause defects in the welded joint (pores, cracks) or its delayed destruction. [6]

III. METODOLOGY

In automatic submerged arc welding, consideration must be given to the saturation of the metal N_2 and H_2. The main source of N_2 in welding is air. Molecular nitrogen dissociates into atoms at high temperatures

$$N_2 = 2N — 711{,}436 \text{ kJ / mol.} \quad (1)$$

Dissociation can occur at welding temperatures, but most of the nitrogen remains in molecular form.
At high temperatures, in the presence of oxygen, nitrogen oxides are also partially formed. In Fe (and iron alloys), nitrogen dissolves and forms chemical compounds - nitrides (Fe_2N and Fe_4N).
At constant temperature, the solubility of nitrogen in liquid metals is determined by the ratios:

$$[\%N] = K_1 p_N ;$$
$$[\%N_2] = K_2 p_{N_2} . \quad (2)$$

where K_1 and K_2 are temperature-dependent coefficients;
P_1 and P_2 are the partial pressures of atomic and molecular nitrogen.
The solubility of nitrogen decreases stepwise during the transition of iron from a liquid to a solid state; nitrides are not formed at these temperatures and the gas tends to leave the solution in the form of a gas phase, which leads to the formation of pores under certain conditions. During welding, the products of decomposition of carbohydrates from fluxes and dissociation of water vapor are sources of hydrogen.
Basically, in welding, hydrogen is always present in the gas phase interacting with the metal.
In the gas phase, hydrogen can be present in the form of ionized atomic and molecular. A significant part of the hydrogen in the arc is dissociated into atoms. Ionization of hydrogen occurs according to the reaction:

$$H_2 = H + H^+ + e - 1745 \text{ kJ / mol.} \quad (3)$$

This reaction is less likely than dissociation into atoms, due to the very large thermal effect.
Fe, Ni, Co, Cu does not form hydrides. These metals adsorb hydrogen in the solid state, which sharply increases the solubility of hydrogen during melting. At a constant temperature for Fe, Ni, Co, Cu, the solubility of hydrogen obeys the following relationships:

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$$\left[\%H\right]=K_1 p_H;$$
$$\left[\%H\right]=K_2 p_{H_2} \quad (4)$$

where K1, K2, K3 are coefficients that depend on temperature;
P_H, P_{H_2} - partial pressures of atomic or molecular hydrogen in the gas phase;
The solubility of hydrogen in iron increases abruptly during the transition from solid to liquid state.
Depending on the partial pressure $P_{H}2$ for liquid iron, the solubility of hydrogen V (ml /100g):

$$\lg V=0{,}5\lg p_{H_2}-\frac{1745}{T}+0{,}888 \quad (5)$$

Even at relatively low pressures in the gas phase, the total hydrogen content in the molten iron can exceed the equilibrium solubility in the solid metal during crystallization.
Removal of hydrogen sources consists in preliminary cleaning of the edges from rust, water oxides, drying from adsorbed water, and electrodes calcination.
Under welding conditions, hydrogen bonding is carried out in OH or in HF. The most common binding in HF is according to the following scheme:

$$2CaF_2+3SiO_2=2CaSiO_3+SiF_4$$
$$SiF_4+3H=SiF+3HF$$
$$SiF_4+2H_2O=SiO_2+4HF \quad (6)$$

The oxidation of the metal leads to a decrease in the content of hydrogen in the metal. Therefore, a well-deoxidized metal is very sensitive to gaseous hydrogen, which requires the use of stronger protective measures, the introduction of fluorides, calcining of fluxes, and so on.
The solubility of hydrogen in metals of this type obeys the distribution law:

$$\left[H\right]=k' p_{H_2}, \quad (7)$$

and the pressure of atomic hydrogen can be found from the following formulas:

$$1/2H_{2(r)}\leftrightarrow\left[H\right];\ K_p=p_H^2/p_{H_2}=f(T);\ p_H=\sqrt{K_p p_{H_2}};\quad \left[H\right]=k_T\sqrt{p_{H_2}} \quad (8)$$

The temperature dependence is determined through the solubility constant:

$$k_T=k_0 e^{-\Delta H/(RT)} \quad (9)$$

Where ΔH is the difference in the enthalpies of dissolution.
Dissolved hydrogen turns out to be undesirable, since it sharply reduces the ductility of steel, causes porosity in welded seams, in the heat-affected zone.
Hydrogen in a solid metal can be in various states:
a) diffusion-mobile hydrogen, which is in the state of an interstitial solid solution. It is relatively free and can leave the metal, diffusing to the interface and desorbing from it during aging. Diffusion-mobile hydrogen can participate in isothermal diffusion described by the equations of Fick's laws, diffusion caused by temperature gradients, mechanical gradients (Konobeevsky's "ascending" diffusion) or electrical stresses ("electrotransport");
b) residual hydrogen - hydrogen adsorbed at the interfaces or in the zone of accumulation of dislocations, reduces their mobility. Diffusion-mobile and residual hydrogen can transform into each other. Residual hydrogen leaves the metal at ~900 K in vacuum;
c) bound hydrogen, which is removed from the metal during vacuum melting, is in the discontinuities of the metal (cavities and pores) in a molecular state. The transition of bound hydrogen to diffusion-mobile is very difficult, since the process of dissociation of H_2 molecules into atoms requires a large expenditure of energy.

IV.CONCLUSION

Scientifically grounded selection of the slag composition in automatic arc welding under a layer of ceramic flux of low-carbon and low-alloy steels makes it possible to reduce the hydrogen content in the weld metal to the required degree:
- binding hydrogen in the gas phase into compounds that are stable at high temperatures,

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- removal and limitation of hydrogen sources during welding;
- a decrease in the solubility of hydrogen in a liquid metal, in particular by its oxidation.

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