Possibilities of Application of Carbon-Fluorine Containing Additions in Submerged-Arc Welding

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Abstract. The paper provides results of comparative analysis of the effect of carbonaceous components introduced into welding fluxes on molten metal – slag interaction. A positive influence of carbonaceous additives on gas content and mechanical properties of welds is demonstrated. Carbon and fluorine containing additives are emphasized to be promising for automatic submerged arc welding.

Introduction

The development of oil deposits in the North regions (in conditions of low temperatures) is connected with the necessity of oil tank manufacture for negative temperature exploitation. According to the “Rules of installation of vertical cylindrical steel tanks for oil and oil products”, Safety rules 03-605-03 and Construction codes 23-81, the increased demands are made on welded joints, with particular attention to the impact strength at negative temperatures. At Russian enterprises submerged-arc welding (SAW) has been widely used, and technological process of assembling, welding, controlling and rolling of tank wall sheets into coils is done on special rolling unit with upper and lower rolling.

Reservoir metal structure plant in Novokuznetsk has developed and mastered the reservoir manufacture technology for oil products for negative temperature exploitation [1 – 4]. In the given technology a two-side welding of butt joints of wall sheets is done automatically in SAW first on the top layer, then, after drawing the sheet by the drum, on the lower layer. To ensure a high productivity in manufacturing, crack formation elimination and to improve the mechanical properties we have developed and patented in Russia [5, 6] a technology of welding for tanks wall sheets. According to the technology a welding of tank is done with the welding wire Sv-08GA under the mixture of fluxes AN-348А and AN-67B with the ratio of 1:1. Welding is done without bevel to the sheet thickness of 16 mm. On the top layer the butt joints are welded at reduced power conditions, ensuring a weld metal penetration up to 0.55 of sheet thickness. On the lower layer welding is done at high power conditions, permitting to get a weld metal penetration up to 0.7 of sheet thickness.

However, the required level of mechanical properties is not always ensured when using some flux grades, namely, the impact strength at lower temperature due to the formation of a large number of nonmetallic inclusions in the welded joints. Most of the nonmetallic inclusions in the joints are oxide, irrespective of whether they are exogenic or endogenic. A content of nonmetallic inclusions in a joint, in turn, depends on the quantity of total oxygen. As the oxygen solubility in a solid metal is small, the total oxygen content in a joint characterizes the level of its contamination by nonmetallic inclusions.
The existing fluxes for low alloy steel welding show the increased total oxygen content, and, consequently, the increased number of nonmetallic inclusions in the joints. Today the reduction of nonmetallic inclusion content in welded joints in automatic SAW is obtained with low oxidizing flux application. But these fluxes have unsatisfactory welding and technological properties and are rarely used in low alloy steel welding. In the case of oxidizing flux application the metal of a joint1) to do the removal of hydrogen at the expense of fluorine containing compounds \{like Na$_3$AlF$_6$; CF$_x$ = 25 – 35 (1≥x>0) etc.\}, disintegrating at temperatures of welding processes with the liberation of fluorine, which, in turn, reacts to hydrogen dissolved in steel with the formation of gaseous compound HF;

2) to carry out the intensive carbon boiling at the expense of CO and CO$_2$ being formed in integration of carbon fluoride CF$_x$ (1≥x>0) with the dissolved oxygen in steel, and as carbon is in a bound state a carbonization of steel should not practically occur;

3) to increase the arc stability at the expense of the elements facilitating the potassium and sodium ionization in the arc column.

![Diagram of installation for rolling of reservoirs with upper (a) lower rolling (b)](image)

**Methodology**

The addition to flux was prepared in the following way: a carbon and fluorine containing components was mixed with glass, and after it a drying, cooling and crushing was done. Then the addition was mixed with a flux in a special mixer in a strictly prescribed ratio. For investigation the flux grades AN -348, AN -60, AN -67 and OK 10.71 were taken as base variant and their mixtures with admixture of flux-additions.

Experiments were carried out on the specimens made from 09Mn2Si steel, 16 mm thick and of size 200x500 mm. Welding of butt joints without edge preparation was done from two sides, as in welding of sheets of walls on the stand for rolling. A wire Sv-08Mn of 5 mm diameter was used as a filler metal.

Submerged-arc welding of specimens was done in identical conditions. Specimens were cut from welded plates and the following investigations were carried out: X-ray spectroscopic analysis of
composition of joint metal, metallographic analysis of welded joints, determination of total oxygen content in joints, mechanical properties, hardness of welded joints and impact toughness of joints at temperatures of 200°C, minus 400°C and minus 700°C.

The metal chemical composition determination of welded joints by carbon, sulphur and phosphorus content was done by chemical methods according to State Standard 12344-2003, State Standard 12345-2001, State Standard 12347-77 respectively. Content of alloying elements in a metal of joint, calcium oxide, sodium and fluorine compounds in fluxes with additions and slags obtained after welding was determined on X-ray fluorescence spectrometer XRF-1800 by SHIMADZU firm.

Results
The test showed that the carbon concentration in a joint corresponding to the carbon concentration in the initial metal (Fig. 2) is insured upon use of carbon and fluorine containing addition in quantity up to 6%.

![Figure 2. Influence of carbon and fluorine containing addition carbon content in welded joint](image)

Figure 2. Influence of carbon and fluorine containing addition carbon content in welded joint

Sulphur and phosphorus content in a metal of joint obtained in submerge-arc welding with additions and without additions did not change and was in the range of \( S = 0.015 \text{ -- } 0.019\% \), \( P = 0.013 \text{ -- } 0.015\% \), i.e. the application of fluxes with additions had no effect on the transition of sulphur and phosphorus from the formed slag into metal.

Determination of oxygen by method of reduction smelting on gas analyzer TC-600 by LECO firm showed that mass fraction of the given gas with the increase of addition content in flux has decreased (Fig. 3), and a fractional gas analysis has showed that depending on a state of oxidation and basicity of a slag system a redistribution of oxygen in inclusions occurs. Distributions of oxygen in silicates, aluminates, alumosilicates is likely to be connected with basicity of the obtained slag and assimilation of nonmetallic inclusions by slag depending on the obtained slag viscosity.
The largest number of aluminates and alumosilicates, effecting adversely the physical and chemical properties of the welded joint, was contained in submerged-arc welding with flux AN -60, when the addition was introduced the decrease in number of these compounds was observed. In fluxes AN -348 and AN -67 the changes were negligible (Fig. 4).

The carbon and fluorine containing addition influenced the reduction of the hydrogen in the welded joint according to the mechanism described above at the expense of fluorine (Fig. 5), and sodium concentration was slightly decreased (Fig. 6).
A metallographic examination of polished microsections of welded joints were done with the help of optical microscope OLYMPUS GX-51 in a light field at magnifications x 100, x 500. Metal microstructure was revealed by etching in a solution of 4% HNO₃ in ethyl alcohol. The structure of base metal of all specimens consists of ferrite grains and lamellar pearlite (4 – 5 mcm). In the transition zone from the base metal to the deposited one a fine-grained structure is observed (1 – 2 mcm), being formed as a result of recrystallization on heating in welding process. Ferrite grains elongated in the direction of heat removal due to heating and accelerated cooling are present in the microstructure of welded joint. A detectable difference in structure of joints welded under different fluxes was not revealed. In specimens welded by submerged-arc welding with carbon and fluorine containing additions a decrease of contamination level by nonmetallic inclusions, connected with the decrease of total oxygen content was observed.

Study of mechanical properties (yield point, strength, unit elongation and impact toughness at negative temperatures) of specimens, cut according to State Standard 6996-66, has shown that a level
of properties exceeds significantly the required values of State Standard 32385-2008 and normative values of Safety Rules 03-605 (rules for manufacture of vertical cylindrical tanks for oil and oil products) and rises with the increase of carbon and fluorine containing addition (Fig. 7). The increase of impact toughness values at negative temperatures (Fig. 8) should be especially noted.

**Conclusion**

Thus, upon introduction of the developed carbon and fluorine containing addition to the fluxes AN-60, AN-67, OK 10.71 the gas saturation of welded joint is increased, contamination by oxide nonmetallic inclusions is decreased, a complex of the required mechanical properties and impact strength (especially at negative temperatures) is enhanced.

The production of carbon and fluorine containing addition protected by the patent [13], is mastered in the conditions of the joint-stock company N.E. Kryukov Novokuznetsk reservoir metal structure plant.

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**Figure 7.** Change of tensile strength depending on quantity of carbon and fluorine containing addition.

**Figure 8.** Change of impact strength depending on quantity of carbon and fluorine containing addition.
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