New Tendencies in Development of Carbonaceous Additives for Welding Fluxes

N A Kozyrev, R E Kryukov, O A Kozyreva

Federal State Budgetary Educational Institution of Higher Professional Education «Siberian State Industrial University», Research and Development Center «Welding Processes and Technologies»
654007, Russia, Novokuznetsk, 42, Kirov str.

E-mail: kozyrev_na@mtsp.sibsiu.ru

Abstract. The paper provides results of comparative analysis of the effect of carbonaceous components introduced into welding fluxes on molten metal – slag interaction. Thermodynamical calculations of dehydrogenization are presented for submerged arc welding. 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 issue of new fluxes and their additives development has been attracting much attention currently, as well as research into their influence on welding and technological characteristics of a weld and on the concentration of oxygen and non-metallic impurities in a weld [1-5].

Submerged arc welding is attended by intensive mass transfer of liquid molten metal and slag, forming from welding flux. Reactions of oxidation and deoxidation of manganese, ferrum, and silicon, i.d. exchange processes involving oxygen are typical for this process. The most grades of domestically produced fluxes, which are applied for welding low-alloyed steels are oxidizing ones and ground on silicon-manganese oxidation-reduction processes. Here, the products of these reactions are oxide compounds of silicon, manganese, ferrum, aluminum etc., which often can’t surface and assimilate to slag, forming from welding flux, the level of impurity of weld metal by non-metallic admixtures increases consequently; as the result, the complex of physical and mechanical characteristics deteriorates. Apparently, restoratives, which form gaseous products of reactions, are advisable to apply in order to avoid impurity of weld metal. It is carbon that can be a restorative of this kind, and forms gaseous compounds CO2 and CO when reacting with oxidizers.

Materials and methods of research

Shielding is usually provided through pushing atmospheric gases aside from weld zone by forming gases CO2 (CO); that helps to reduce or even exclude the probability of molten metal saturation with oxygen, nitrogen or hydrogen from atmosphere. Gas-forming compounds of carbonates like CaCO3, MgCO3, FeCO3, MnCO3 and their derivatives are usually used for this purpose. Gas shielding is
possible due to CO₂ as high-temperature decomposition of carbonates takes place according to the following reactions and temperatures [6]:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad (900-1200 \, ^\circ\text{C}), \\
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2 \quad (>650 \, ^\circ\text{C}), \\
\text{FeCO}_3 & \rightarrow \text{FeO} + \text{CO}_2 \quad (280-490 \, ^\circ\text{C}), \\
\text{MnCO}_3 & \rightarrow \text{MnO} + \text{CO}_2 \quad (330-500 \, ^\circ\text{C})
\end{align*}
\]

According to stoichiometric calculations the results of decomposition are as follows: 1 kg CaCO₃ – 0.224 m³ CO₂, 1 kg MgCO₃ – 0.267 m³, 1 kg FeCO₃ – 0.192 m³, 1 kg MnCO₃ – 0.194 m³.

Here CO₂ emits at high pressure of off-gases.

In terms of Mendeleev – Clapeyron law at 1600 °C (1873K) the pressure of CO₂ is

\[
p = \frac{m \cdot RT}{V \cdot M}
\]

According to equation (5) CO₂ pressure is 694.84 kPa for CaCO₃, 688.93 kPa for MgCO₃, 698.26 kPa for FeCO₃, and 696.54 kPa for MnCO₃.

Without taking into account the costs of carbonates decomposition, MgCO₃ and CaCO₃ are the most optimal components, which help to get most CO₂ when decomposing 1 kg of material, succeeded by MnCO₃ and FeCO₃.

Furthermore, when decomposing CaCO₃ and MgCO₃ basic oxides CaO and MgO are formed and improve basicity of welding flux, and that of a forming slag, respectively, whereas, when MnCO₃ and FeCO₃ decomposing oxides FeO and MnO are formed, which raise the degree of oxidation in slag systems and oxygen concentration in a weld. The latter causes all negative consequences – increasing level of impurity by non-metallic oxide components in a weld and deterioration of mechanical properties.

Having followed all mentioned pre-conditions we have developed a flux – ANK additive, protected it by a patent of the Russian Federation and applied in production process at Open Joint Stock Company “Novokuznetsk Plant of Reservoir Metalware named after N.E. Kryukov” [7]. For its manufacturing ferrosilicon FS75 (GOST 1415-78), marble M92-97 (GOST 4416-73 (92-97% CaCO₃)), and liquid glass (GOST 13078-81) were used. Production technology was as follows. Marble and ferrosilicon were ground to less than 1 mm fraction. Grinded marble and silicon were mixed in 50 to 50% mass proportion. It was dried at temperature 100-200 °C for 10 - 20 minutes, succeeded by grinding and size grading to 2.5 mm. 3-5% of additive was introduced into fluxes. Before a flux with an additive is used its 40 – 60 minutes annealing in the furnace is recommended at temperature 250-350 °C.

This additive is used for roll welding of tanks. The technology involves assembling, welding, controlling and rolling plates of tanks walls, all the processes are performed on special roll facilities with upper and down rolling. Two-side submerged arc welding of butt joints of wall plates is applied in the process, first on the upper tier, then on the lower one, after the plate is rolled. An additive helped to avoid pore formation and improve quality of welds.

However, shielding gases CO and CO₂ can form due to carbon, added to the flux, according to the reactions:

\[
\begin{align*}
\text{(C)} + \frac{1}{2} \text{[O₂]} & = \{\text{CO}\}, \\
\text{(C)} + \text{[O₂]} & = \{\text{CO₂}\}
\end{align*}
\]

Here 1.863 m³ CO₂ and 1.864 m³ CO release per each kg of carbon (in normal conditions), and design pressure of gases is 311.66 kPa for CO₂ and 694.84 kPa for CO at 1600 °C.

The second important issue is that of weld metal dehydrogenization. As a rule, it is carried out by introducing fluorine-containing additives (fluorite or cryolite), hydrogen combines with fluorine and is further removed as a compound HF.

The following chemical transformations can be considered as probable reactions of removal:

\[
\frac{1}{2} \text{(CaF₂)} + \text{[H]} + \frac{1}{2} \text{[O]} = (\text{CaO}) + \text{H F₈},
\]

(8)
\[
\frac{1}{6}(\text{Na}_3\text{AlF}_6) + [\text{H}] + \frac{1}{2} [\text{O}] = \frac{1}{6}\text{NaAlO}_2_s + \text{HF} + (\text{Na}_2\text{O}) , \quad (9)
\]

As well as reactions:

\[
2(\text{CaF}_2) + 3(\text{SiO}_2) = 2\text{CaSiO}_3_s + \text{SiF}_4_g , \quad (10)
\]

\[
\frac{2}{3}(\text{Na}_3\text{AlF}_6) + \frac{5}{3}(\text{SiO}_2) = \text{SiF}_4_g + \frac{2}{3}\text{NaAlO}_2_s + \frac{2}{3} (\text{Na}_2\text{SiO}_3), \quad (11)
\]

succeeded by reactions of dehydrogenization with SiF\(_4\):

\[
\frac{1}{2} \text{SiF}_4_g + [\text{H}] = \frac{1}{2}\text{SiF}_2 g + \text{HF}_g \quad (12)
\]

\[
\frac{1}{4} \text{SiF}_4_g + [\text{H}] + \frac{1}{2} [\text{O}] = \frac{1}{4} (\text{SiO}_2) + \text{HF}_g \quad (13)
\]

\[
\frac{1}{3} \text{SiF}_4_g + [\text{H}] = \frac{1}{3}\text{SiF}_g + \text{HF}_g \quad (14)
\]

\[
\frac{1}{2} \text{SiF}_4_g + [\text{H}] = \frac{1}{2} \text{SiF}_2 g + \text{HF}_g \quad (15)
\]

Thermodynamical characteristics in standard conditions [\(\Delta H^o(T), \Delta S^o(T), \Delta G^o(T)\)] needed to assess reaction probability were calculated by well-known methods [8] in the temperature range of welding processes 1700 – 2200 K [9] in terms of thermodynamic properties of reagents [\(\Delta H^o(T)-\Delta H^o(298,15 K), \Delta S^o(T), \Delta G^o(298,15 K)\)] [10,11]. Here, chemical states \(\text{Na}_3\text{AlF}_6l, \text{SiO}_2l, \text{SiF}_4g, \text{NaAlO}_2 s, \text{Na}_2\text{SiO}_3l, \text{CaF}_2s, \text{CaSiO}_3 s, \text{H}_2g, \text{SiF}_2g, \text{HF}_g, \text{O}_2g, \text{SiF}_g, \text{H}_g\) were selected as standard ones for substances – reagents in the range 1700 – 2200 K according to fact aggregate states of phases in the system under consideration.

The results of calculations are provided in the Table. The graphs of standard Gibbs energy reactions (8) - (11) according to temperature are depicted in Figure 1, those of reactions (12) - (15) in Figure 2.

| Reaction | \(\Delta G^o(T), \text{kJ} \) |
|----------|-----------------------------|
|          | 1700K | 1800K | 1900K | 2000K | 2100K | 2200K |
| 8        | -16.22 | -18.61 | -20.93 | -23.17 | -25.36 | -27.47 |
| 9        | -32.32 | -33.82 | -35.20 | -36.46 | -37.62 | -38.68 |
| 10       | -41.80 | -35.98 | -30.62 | -25.71 | -21.22 | -17.18 |
| 11       | -82.41 | -76.11 | -70.40 | -65.22 | -60.56 | -56.38 |
| 12       | -86.62 | -78.13 | -69.68 | -61.27 | -52.90 | -44.57 |
| 13       | -90.16 | -89.83 | -89.51 | -89.21 | -88.91 | -88.63 |
| 14       | -113.04 | -104.93 | -96.86 | -88.82 | -80.80 | -72.82 |
| 15       | -38.07 | -40.60 | -43.08 | -45.49 | -47.84 | -50.14 |

Figure 1. Standard Gibbs energy of reactions (8) - (11)
Figure 1 demonstrates that reaction (9) is thermodynamically the most probable (cryolite dehydrogenization), the second one is reaction (8) (fluorite dehydrogenization), followed by reactions (10, 11), where silicon tetrafluoride is formed as an intermediate product of further reactions (12) - (15); the latter result in formation of gaseous compound HF. Here, reaction (13) is thermodynamically the most probable (SiF₄ combines with hydrogen and oxygen). The stoichiometric reactions (15), (12), (14) are the least probable ones.

Therefore, Na₃AlF₆ is the most reasonable to use for dehydrogenization when submerged arc welding as if compared with fluorite.

Having taken into account the aforementioned preconditions, we have developed a technology of submerged arc welding with carbonaceous additives. As the basis of carbon and fluorine containing additive we took metallurgical production wastes. It was dust with the following chemical composition (mass %): Al₂O₃ = 21 – 46.23; F = 18 – 27; Na₂O = 8 – 15; K₂O = 0.4 – 6; CaO = 0.7 – 2.3; SiO₂ = 0.5 – 2.48; Fe₂O₃ = 2.1 – 3.27; C = 12.5 – 30.2; MnO = 0.07 – 0.9; MgO = 0.06 – 0.9; S = 0.09 – 0.19; P = 0.1 – 0.18.

Mineralogical makeup of dust was determined according to the data of X-ray structural analysis made by diffractometer DRON-2 in the mode: Fe – Kα radiation, voltage 26 kV, electrical current 30 mA.

The research into the dust of electrostatic precipitators revealed that the material consisted of bi-dimensionally ordered carbon (dₒ₂=3.47Å, Lₓ=45.8Å), X-ray amorphous substance, cryolite, corundum, hyolith, and various admixtures. Diffraction patterns of roasted at 700°C material demonstrate no indication of graphite, that is caused by nearly complete burning out of carbon-containing mass in this temperature range, as well as significant curve flattening on the diffraction pattern, and decrease in X-ray amorphous substance. The reason of the latter is probably chemical composition of X-ray amorphous substance, which carbon compounds are main components of. At 700°C the change in indication intensity of mineralizing components (cryolite, corundum, X-ray amorphous substance, fluoride, hematite and various admixtures) was recorded.

From the theoretical point of view the additive makes possible: 1) dehydrogenization by fluorine-containing compounds (like Na₃AlF₆), decomposing at the temperatures of welding processes and isolating fluorine, which combines with dissolved in steel hydrogen and forms gaseous HF; 2) intensive carbon “boiling” due to forming CO and CO₂, when fluoric carbon CFₓ (1 ≥ x > 0) combines with dissolved in steel oxygen, here, as carbon is in a bound state steel carbonization is hardly possible; 3) improvement of arc stability due to potassium and sodium, facilitating ionization in arc column.

To make an additive to flux carbon and fluorine containing substance was mixed with liquid glass, then this mixture was dried, cooled down and grinded. Afterwards this additive was mixed with flux in
a special mixer according to a definite, strictly determined proportion. AN-348A, AN-60, AN-67 fluxes were taken as basic ones and their mixtures with flux-additives.

The experiments were carried out on 200×500 mm 09G2S steel samples 16 mm in thickness. Fay welding of butt joints was made on two sides, as when welding wall plates of tanks on roll facility. Sv-08GA wire 5 mm in diameter was used as a filler metal.

Submerged arc welding of samples was made in similar modes. The samples were cut of welded plates and subject to the following tests: X-ray spectral analysis of weld metal chemical composition, metallographic tests of welds; total concentration of oxygen in welds, mechanical properties, strength of joint welds and impact strength of welds were determined at temperatures -20°C and -40°C. Concentration of carbon, sulphur, phosphorus was determined in chemical composition of weld metal by chemical methods in terms of GOST 12344-2003, GOST 12345-2001, and GOST 12347-77, respectively. Concentration of alloying elements in weld metal; that of calcium oxide, silicon, manganese, aluminum, magnesium, ferrum, potassium, sodium and fluorine-compounds in fluxes with additives and slag, obtained after welding was determined by SHIMADZU roentgen-fluorescent spectrometer XRF-1800.

The experiments demonstrated that maximum 6% carbon and fluorine containing additive provided carbon concentration in weld similar to its concentration in original metal (Figure 3), whereas concentration of oxygen, hydrogen and nitrogen dropped (Figures 4, 5, 6).

Metallographic research into polished sections of joint welds was carried out by optical microscope OLYMPUS GX-51 in bright field and zooming ×100, ×500. The microstructure of metal was found out by etching in 4 % HNO₃ solution in ethanol. The structure of base metal in all samples consists of ferrite grains and lamellar pearlite (4-5 µm). In base – to – added metal zone a fine-grain structure occurs (1-2 µm), which was formed as the result of re-crystallizing when heating in course of welding. In the microstructure of a weld there are ferrite grains stretched towards heat rejection because of heating and speeded up cooling down. Structures of welds didn’t differ much irrespectively of used fluxes. The level of impurity by non-metallic substances decreased in samples, which were welded with fluxing agents, containing carbon and fluorine additives; it was caused by reduction of total oxygen concentration.

The research into mechanical properties (yield point, strength, modulus of elongation, impact strength at temperatures below zero) carried out on cut according to GOST 6996-66 samples, demonstrated that the level of properties went beyond the values required in GOST 31385-2008 and increased as the concentration of carbon and fluorine containing additive rose. Increasing impact strength KCV and KCU at temperatures -20°C and -40°C, respectively (Figures 7, 8) is worth mentioning. Flux-additives, which were developed, have been protected by the Russian Federation patents [12, 13].

Figure 3. Influence of carbon and fluorine containing additive on carbon concentration in a weld
Figure 4. The change in oxygen in dependence on carbon and fluoride containing additive concentration

Figure 5. The change in hydrogen in dependence on carbon and fluorine containing additive

Figure 6. The change in nitrogen in dependence on carbon and fluorine containing additive
Conclusions

1. On the ground of made calculations and carried out experiments we can conclude that carbon containing additives to welding fluxes are possible and promising ones in order to improve welding and technological characteristics of welded metalware.

2. The probability of dehydrogenization of a weld in fluorine containing submerged arc welding has been assessed thermodynamically in the temperature range 1700 – 2200 K. Here, Na₃AlF₆, SiO₂, SiF₄, NaAlO₂, Na₂SiO₃, CaF₂, CaSiO₃, SiF₄, H₂, SiF₂, H₂O, SiF₆, H₂, were selected as standard states for substances - reagents. In terms of calculation of standard Gibbs energy reactions it has been found out that the reaction of gaseous hydrogen fluorine direct formation by cryolite is thermodynamically the most probable one, the second probable is the group of reactions resulting in formation of silicon tetrafluoride as an intermediate product for further HF formation. In this group the most thermodynamically probable reaction is that of SiF₄ with hydrogen and oxygen. In terms of calculations Na₃AlF₆ is more reasonable to use for dehydrogenization when submerged arc welding in comparison to fluorite.

3. Introduction of developed carbon and fluorine containing additive into fluxes AN-348A, AN-60
and AN-67 reduces gas content of a weld, the level of impurity by oxide non-metallic substances, and improves required mechanical properties and impact strength (at temperatures below zero, especially).

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