Some Aspects of Oxidation-Reduction Reactions under Carbon-Bearing Flux Welding

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Abstract. The authors have completed thermodynamic calculations of oxidation-reduction processes under submerged arc welding with application of carbon containing additive. The calculations have shown that carbon, due to its high reducing properties under T = 1950 – 2200 K, introduced into the system can significantly decrease the amount of non-metallic inclusions in the weld metal and so improve its mechanical properties.

Introduction

Flux welding is associated with intensive mass transfer processes between the molten metal and slag formed out of the welding flux. The process is accompanied by the oxidation-reduction reactions of manganese, iron and silicon, i.e. oxygen involving transfer processes. Currently most grades of domestic fluxes applied for low-alloy steel welding are oxidizing and are based upon the principles of silicon-manganese oxidation-reduction processes. The resultants of the given reactions are the oxides of manganese, silicon, iron, aluminum, etc. which normally lag to come to the surface to be assimilated by the slag formed from the welding fluxes and this increases weld metal contamination with non-metallic inclusions leading to significant reduction of physical and mechanical properties. To avoid weld metal contamination it seems reasonable to use reducing agents forming reaction gases. Such reducing agent can be carbon which forms gaseous compounds CO_2 and CO when reacting with oxidizers.

We estimated the thermodynamic probability of reactions (1) – (24) which result in reduced non-metallic inclusions containment in the weld metal. The reducing properties of carbon were compared to those of other reducing agents in the studied system of liquid weld metal – oxide melt – gas:

$$(FeO) + [Mn] = [Fe] + (MnO), \quad (1)$$
$$(FeO) + 1/2[Si] = [Fe] + 1/2(SiO_2), \quad (2)$$
$$(FeO) + C_{(solid)} = [Fe] + CO_{(gas)}, \quad (3)$$
$$(FeO) + 1/2C_{(solid)} = [Fe] + 1/2CO_{2(gas)}, \quad (4)$$
$$(FeO) + CO_{(gas)} = [Fe] + CO2g, \quad (5)$$
$$(FeO) + 2/3[Al] = [Fe] + 1/3(Al_2O_3), \quad (6)$$
$$(MnO) + 1/2[Si] = [Mn] + 1/2(SiO_2), \quad (7)$$
$$(MnO) + [Fe] = [Mn] + (FeO), \quad (8)$$
$$(MnO) + C_{(solid)} = [Mn] + CO_{(gas)}, \quad (9)$$

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$$(MnO) + 1/2C_{(solid)} = [Mn] + 1/2CO_{2(gas)}, \quad (10)$$
$$(MnO) + CO_{(gas)} = [Mn] + CO2g, \quad (11)$$
$$(MnO) + 2/3[Al] = [Mn] + 1/3(Al_2O_3), \quad (12)$$
$$(SiO_2) + 2[Mn] = [Si] + 2(MnO), \quad (13)$$
$$(SiO_2) + 2[Fe] = [Si] + 2(FeO), \quad (14)$$
$$(SiO_2) + 2C_{(solid)} = [Si] + 2CO_{(gas)}, \quad (15)$$
$$(SiO_2) + C_{(solid)} = [Si] + CO_{2(gas)}, \quad (16)$$
$$(SiO_2) + 2CO_{(gas)} = [Si] + 2CO_{2(gas)}, \quad (17)$$
$$(SiO_2) + 4/3[Al] = [Si] + 2/3(Al_2O_3), \quad (18)$$
$$(Al_2O_3) + 3/2[Si] = 2[Al] + 3/2(SiO_2), \quad (19)$$
$$(Al_2O_3) + 3[Fe] = 2[Al] + 3(FeO), \quad (20)$$
$$(Al_2O_3) + 3[Mn] = 2[Al] + 3(MnO), \quad (21)$$
$$(Al_2O_3) + 3C_{(solid)} = 2[Al] + 3CO_{(gas)}, \quad (22)$$
$$(Al_2O_3) + 3/2C_{(solid)} = 2[Al] + 3/2CO_{2(gas)}, \quad (23)$$
$$(Al_2O_3) + 3CO_{(gas)} = 2[Al] + 3CO_{2(gas)}, \quad (24)$$

The thermodynamic characteristics of reactions (1) – (24) necessary for reducing properties assessment under the standard conditions [ΔrH°(T), ΔrS°(T), ΔrG°(T)] were calculated by the known methods [1] in the interval of welding processes temperature of 1700 – 2200 K according to the thermodynamic properties of the reagents [[H°(T)- H°(298,15 K)], S°(T), ΔfH°(298,15 K)] taken from the reference books [2, 3].

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The following states $FeO_{(liquid)}$, $MnO_{(liquid)}$, $SiO_{2(liquid)}$, $Al_2O_{3(liquid)}$, $Al_{(liquid)}$, $Si_{(liquid)}$, $C_{(solid\ graphite)}$, $Mn_{(liquid)}$, $Fe_{(liquid)}$, $CO_{(gas)}$, $CO_{2(gas)}$ were chosen as standard for the reacting substances according to the real aggregate state of the phases in the studied system.

The calculated standard Gibbs energies of the reactions are provided in Table 1 and in Figures 1 – 4.

The analysis of the table data and diagrams shows that the highest reduction activity in the system is demonstrated by Al, C, Si. The reducing ability of silicon decreases as the temperature grows and the reducing ability of silicon increases with the growth of temperature. As a result carbon demonstrates stronger reducing ability than silicon at temperatures over T ≈ 1940 K corresponding to the lower limit of the temperature interval in the weld pool under automatic submerge-arc welding (1973 – 2133 K) [4]. Manganese as a reducing agent can be efficient only for iron oxide in the temperature interval up to 1800 K. Over this temperature the reducing ability of carbon exceeds that of manganese.

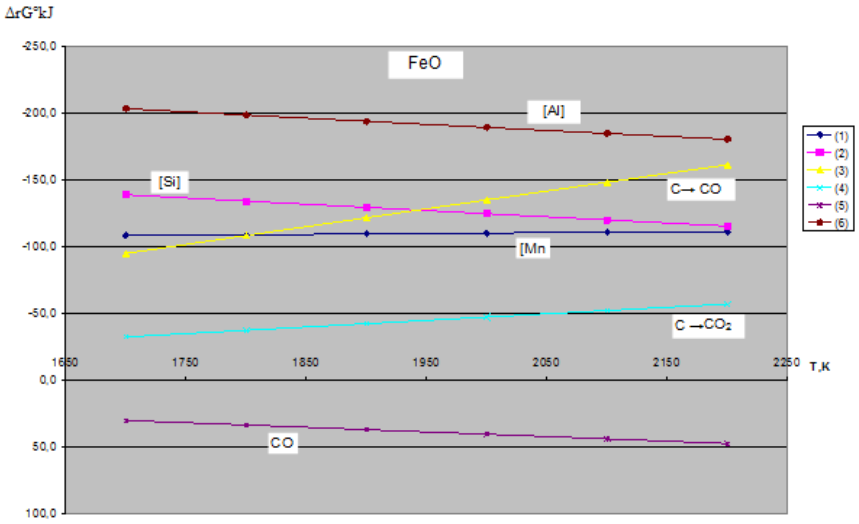


Figure 1. Temperature dependence of standard Gibbs energy of reactions (1) – (6)

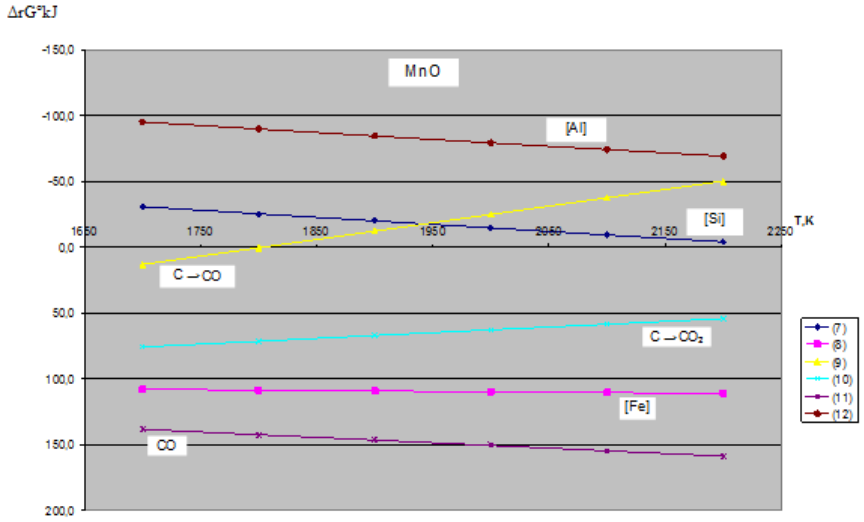


Figure 2. Temperature dependence of standard Gibbs energy of reactions (7) – (12)

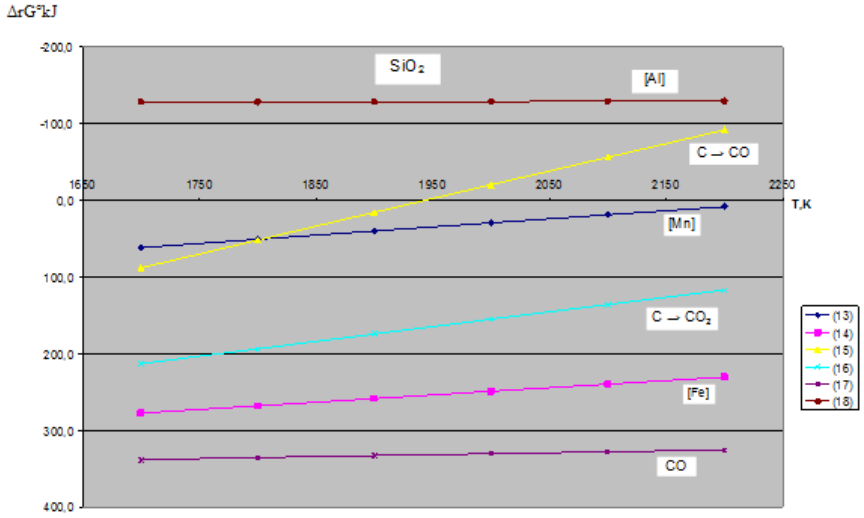


Figure 3. Temperature dependence of standard Gibbs energy of reactions (13) – (18)

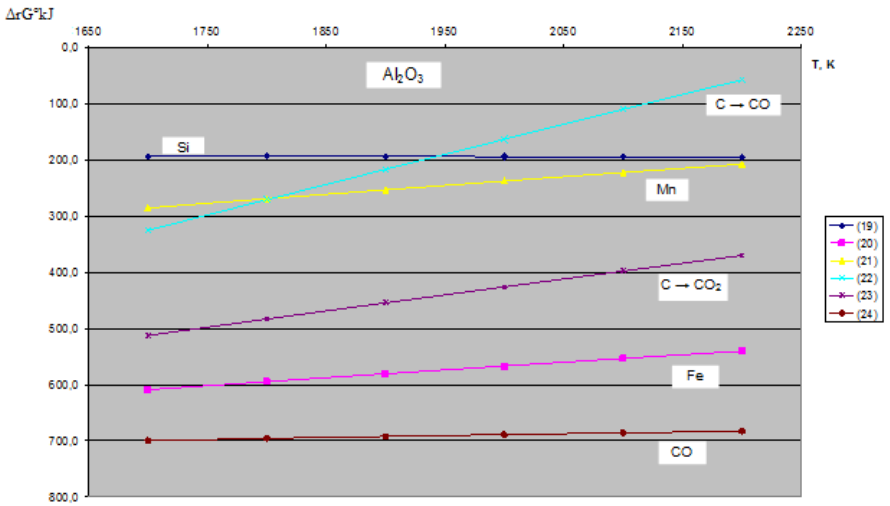


Figure 4. Temperature dependence of standard Gibbs energy of reactions (19) – (24)

Under the temperature over 2200 K aluminum can be formed in the weld metal as a result of reaction between Al_2O_3 oxide with carbon (reaction 22). Under these conditions $\Delta rG°(22) \approx 0$ we can expect that equilibrium constant of the reaction:

$$K = \frac{P_{CO}^3 \cdot a_{[Al]}^2}{a_{(Al_2O_3)}}, \tag{25}$$

(where P_{CO} – equilibrium partial pressure CO in the gas phase; $a_{[Al]}$ – activity of aluminum in the liquid weld metal; $a_{(Al_2O_3)}$ – activity of aluminum oxide in the oxide melt) becomes close to one. Under such equilibrium constant activity of aluminum in the weld metal and, thus, its concentration will be largest for the considered system and the reducing role of aluminum may be important. Aluminum is the best reducing agent for all oxides in the system but it can be formed in the weld metal only in small quantities, thus, concentration of aluminum oxide formed in this case in reactions (6), (12), (18) will be insignificant.

Works [5-14] provide the studies of the influence of carbon-fluorine-containing flux additive upon the process of weld metal refining and weld metal properties. The experiments were completed for the samples from steel 09G2S 16 mm thick 200×500 mm in size. Production of double square butt welds was completed in the same way as that of sheets for tank shells at the rolling stand. Sv-08GA wire 5 mm in diameter was used as additive material. Welding of samples under fluxes was completed under similar welding conditions. Samples were cut out of the welded sheets and the following tests were completed: X-ray spectral analysis of the weld metal composition, metallographic study of the welds, determining general oxygen content in the welds, determining mechanical properties and impact strength of the welds under the temperatures -200 C and – 400 C. The chemical analysis of the welds for carbon was completed according to National State Standard 12344-2003.

The experiments showed that application of up to 6% of carbon-fluorine-containing additive provides concentration of carbon in the weld similar to that in the base metal (Figure 5).

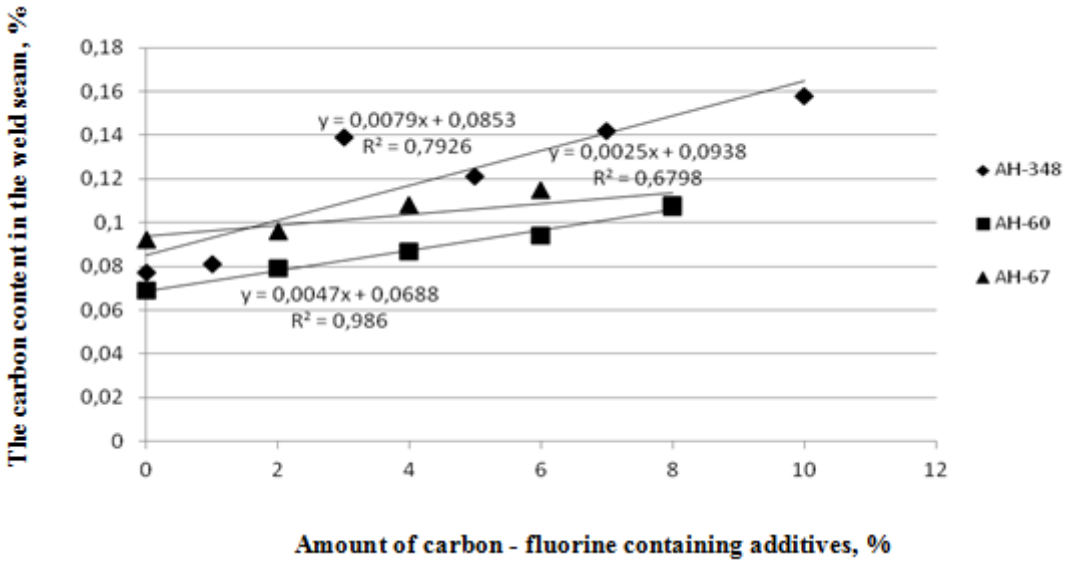
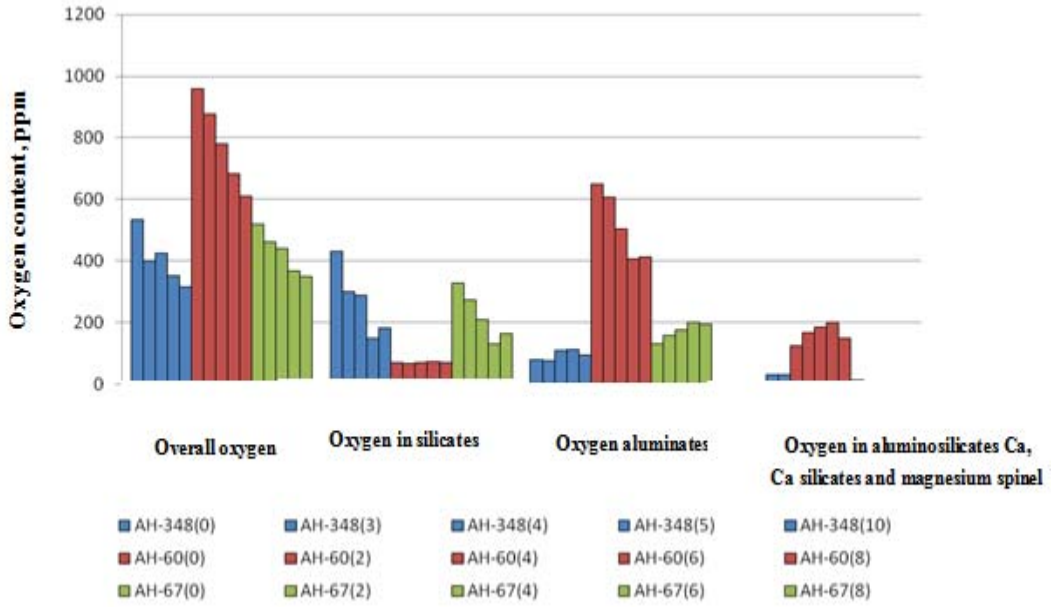


Figure 5. Influence of carbon-fluorine-containing additive upon carbon content in the weld

Determining the oxygen by the method of reduction melting on the gas analyzer “LEGO” TC-600 showed that the weight ratio of the given gas decreased with the growth of additive in the flux (Figure 6). The completed fraction analysis showed that oxygen redistribution in the inclusions depends upon degree of oxidation and basicity of the slag system. The largest percentage of aluminates and aluminum silicates which are detrimental to the physical and chemical properties of the weld joint was

observed under flux AH-60 welding but introduction of the additive reduced their amount. The changes under AH-348 and AH-67 fluxes welding were insignificant.



Note: *- the information in brackets specifies the content of carbon-fluorine-containing additive
Figure 6. Changes of concentration of general and fractional oxygen depending upon the amount of carbon-fluorine-containing additive

Metallographic bright-field examination of polished microslices of the weld joints were completed with optical microscope OLYMPUS GX-51 under the magnifications by ×100, ×500. The microstructure of metal was revealed by etching in the solution of 4% HNO_3 in ethanol. The basic metal structure of all samples consists of ferrite grains and lamellar pearlite (4-5 μ). In the interface region from the basic to the weld metal fine grained structure (1-2 μ) formed after recrystallyzing due to the heating in the process of welding. The structure of welds completed under various fluxes did not show noticeable differences.

In the samples welded under fluxes with carbon-fluorine-containing additives we observed lower amount of non-metallic impurities due to the general decrease of general amount of oxygen. Study of mechanical properties (flow limit, strength, percentage of elongation and impact strength under subzero temperatures) of the samples cut according to National State Standard 6996-66 showed that the properties improved significantly. As a result we observed lower amount of non-metallic inclusions and that of general oxygen in the weld joint as the amount of carbon-fluorine-containing additive in the flux increases.

Conclusions

Thus, the thermodynamic analysis of reactions in the system of molten weld metal – molten oxide – gas proved that, due to its high reducing properties under T = 1950 – 2200 K, carbon introduced into the system can significantly decrease the amount of non-metallic inclusions in the weld metal and so improve the complex of mechanical properties and impact strength (especially under subzero temperatures).

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