INFLUENCE OF K_2ZrF_6 AND SiO_2 ON REFINING ABILITY OF FLUX FOR MANUFACTURING BIMETALLIC CASTINGS

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Abstract. Bimetallic material is considered as an advanced functional material due to the unique physical and mechanical properties varied over the layers. Formation of bimetallic castings with steel base greatly depends on diffusion coupling with the second material working layer at elevated temperatures. The common technological problem is to remove the oxide films from the solid steel surface while its heating prior pouring melt of the working layer. This work studies the protective refining fluxes matching the selected requirements of good wetting the surfaces of solidified metal, effective protection against oxidation in the working temperature range, easy separation after pouring liquid metal and high refining capacity for oxides. The most effective fluxes based on $Na_2B_4O_7$ and B_2O_3 compounds were used. To improve their ability to enhance wetting, work of adhesion and reduce surface decarbonization addition of K_2ZrF_6 and SiO_2 to the flux in the amount of 3-4 wt.% was proposed and investigated. It was established that such additions increased wettability up to 9 and 20%, respectively and reduced the average rate of decarburization in the temperature range from 800 to 1000 ºC on 57 and 37%. The complete reduction of iron from scale on the steel surface was observed, while in the case of $Na_2B_4O_7$ – B_2O_3 system it achieved 30-40% only. The mechanism explaining such a result is proposed to be due to the prevailing effect of zirconium in protecting the surface of the steel base from the oxidation and decarburization. The important result of the study is the recommendation of optimal flux composition (wt.%): $Na_2B_4O_7$ – from 60 to 80; B_2O_3 – from 10 to 30; K_2ZrF_6 - from 3 to 4; SiO_2 from 3 to 4. Thus, such flux could improve the production of steel based bimetallic castings and increase their properties.

Keywords: bimetallic casting, steel, base, surface, temperature, oxides, flux, coating, wetting.

Introduction

There are known methods for producing high-quality steels by modifying them with nitrogen and vanadium [1] and optimizing the modification process [2]. However, for a comprehensive improvement of casting properties under abrasive wear, their production by bimetallic casting seems promising [3].

The process of bimetallic casting consists of the manufacture of a steel base, pouring a working layer and providing their diffusion coupling at elevated temperatures [4]. The formation of oxide films on hot steel surface before its interaction with the melt of the working layer is a common problem.

The films significantly hinder the diffusion interaction of metal layers and complicate the formation of a reliable transition zone between the steel base and the working layer of another metal.

Therefore, ensuring reliable protection of the base surface from oxidation before the start of interaction with the melt of the working layer is a necessary requirement for high-quality bimetallic casting production. The protective atmosphere or vacuum first applied were later found to be impractical and economically unjustified due to a significant increase in the product cost, complications and a decrease of the technological process productivity [5].

The fluxes and synthetic slag are known to create protective and temperature-resistant coatings on the surface of alloys and steel [6], remove some of the oxides [7-9] during heat treatment [10] and at welding [11]. It was established that synthetic multicomponent oxidic systems influence the selected grades of steel and partly protect them from oxidation [6]. Usage of flux coating containing KxAlFy for different Al alloys inhibits the formation of the oxide layer over the surface [7], in case of contact to Cu surface it prevents the formation of the metallic bond between copper and aluminum [8]. In Fe containing bimetal flux interlayer improved the bonding area and interfacial bimetal structure [9]. Some effect in removing oxides is achieved at heating steels in salt bath [10]. It was reported that depending on the flux composition different oxidizing power of flux is achieved to influence the element transfer during submerged arc welding [11].

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The analysis of known fluxes showed that the most rational for bimetallic casting is to use $Na_2B_4O_7$ based fluxes, which is a chemical compound of $Na_2O\cdot2B_2O_3$ and B_2O_3.

When such fluxes cover a heated metal surface, B_2O_3 interacts with iron oxides and converts them into $Fe_nO_m\cdot B_2O_3$ assimilated by the flux [5, 9]. At heating Na_2O up to 1600 ºC it dissociates with formation the following components (vol.%): O_2 from 20 to 19.48; Na from 80 to 78.74; NaO from 0.01 to 0.8; Na_2O from 0.015 to 0.95 [12]

Sodium interacts with iron oxides and reduces iron in the temperature range from 0 to 1190 ºC according to the following reaction:

$$Fe_nO_m + 2mNa = nFe + mNa_2O \tag{1}$$

The high adhesion of fluxes to the steel base is one of the main conditions for their effective performance in the production of bimetallic castings. The work of adhesion (W_a) depends on the specific surface energy on the liquid flux-gas interface (σ_{lg}) and on the contact angle (Θ) (Eq. 2) [13]. Liquid flux completely wets the surface of the solid base at $\Theta = 0$ and there is no wettability at $\Theta = 90^\circ$.

$$W_a = \sigma_{\lg} \cdot (1 + \cos\Theta), \tag{2}$$

$$\cos\Theta = (\sigma_{sg} - \sigma_{sl}) / \sigma_{\lg}, \tag{3}$$

where σ_{sg}, σ_{sl} – specific surface energies on the solid-gas and solid-liquid flux interface, respectively.

The analysis of equations 2, 3 shows that a decrease in σ_{lg} leads to increase in the base surface wettability and the adhesion work by liquid flux.

The disadvantage of Na_2O-B_2O_3 system fluxes is the insufficient protection of the heated surface from interaction with atmospheric oxygen, since this flux contains no components that can react with air oxygen and low wettability of the solid steel surface. This does not allow effectively removing oxides from the surface, its protection from oxidation and in addition leads to decarburization of the steel.

The last happens according to the following reactions:

$$2Fe_nO_m + mC = 2nFe + mCO_2, \tag{4}$$

$$Fe_nO_m + mC = nFe + mCO, \tag{5}$$

As it was shown in [6] additives of K_2ZrF_6 and SiO_2 effectively reduce the surface energy on the liquid Na_2O - B_2O_3 flux and gas interface and should increase the surface wettability and work of adhesion.

The purpose of this article is to study the process of steel oxidation and the influence of K_2ZrF_6 and SiO_2 on wettability, decarburization and the efficiency of removing oxides from the steel surface by fluxes of the Na_2O – B_2O_3 system and to determine the optimal composition of the flux system Na_2O– B_2O_3 – K_2ZrF_6 – SiO_2.

Materials and methods

The study of the oxidation process of main elements of steel (Fe, C, Si, Mn) that form the basis of bimetallic castings and the interaction of the components of synthetic fluxes was carried out by analyzing the calculations of the Gibbs free energy of reactions in the temperature range from 900 to 1300 ºC according to the method given in [14]. This method allows carrying out calculations of the sum of the Gibbs free energies of the initial substances reacted and the products. Based on their differences a linear graph of the change in the free Gibbs energy of the reaction is constructed. In the case of several reactions, the most probable reaction has minimum value of the Gibbs free energy. The initial data for calculations are given in [15; 16].

To confirm the results of thermodynamic calculations, the composition of oxides on the surface of the base of 40L steel containing (wt.%): 0.42 C; 0.2Si; 0.4 Mn were analyzed by DRON-2 X-ray diffractometer. The cylindrical samples with a diameter of 20 mm and a height of 15 mm were preliminary oxidized at a temperature of 1000 ºC with a holding time of 30 seconds. Diffraction spectra were obtained in monochromatic Cu_{kl} radiation. The periods of elementary crystal lattice, phase components and the mass fraction of phases were determined.

The wettability of the metal base was estimated by the area of the flux spread over the steel substrate. The research was conducted on the samples of 40L steel with a diameter of 75 mm and a thickness of 15 mm. A 5 g of powdered flux was placed on the sample and heated by the inductor to a temperature of 1100 °C in the air atmosphere. The flux spreading area was determined using computer processing of the images.

The effect of the protective coatings on decarburization was determined on carbon steel plates with a carbon content of 1.33%. The length of the plates was of 70 mm, the width was of 20 mm, and the thickness was of 1.4 mm. The plates coated with flux were heated to 800 and 1000 °C from 2 to 10 min under air. The carbon content was determined by the JY50E express analyzer.

The temperature was measured with Pt-Pt/Rh thermocouples welded to the samples and four-channel modules WAD-AIK-BUS through the RS-485 interface.

The microstructure of the samples of 20x20x10 mm in size was studied using MIM-10 optical microscope. Determination of decarbonized layer depth was made in accordance with the requirements of [17]. The structural phases were identified by chemical etching of the samples in an alcohol solution with a mass fraction of nitric acid of 2-4%.

Mathematical processing of the experimental data was carried out using the least squares method, with a probability of 95%.

Results and discussion

It was found that the scale of 5 μm in average thickness is formed on the steel surface (Fig. 1 a).

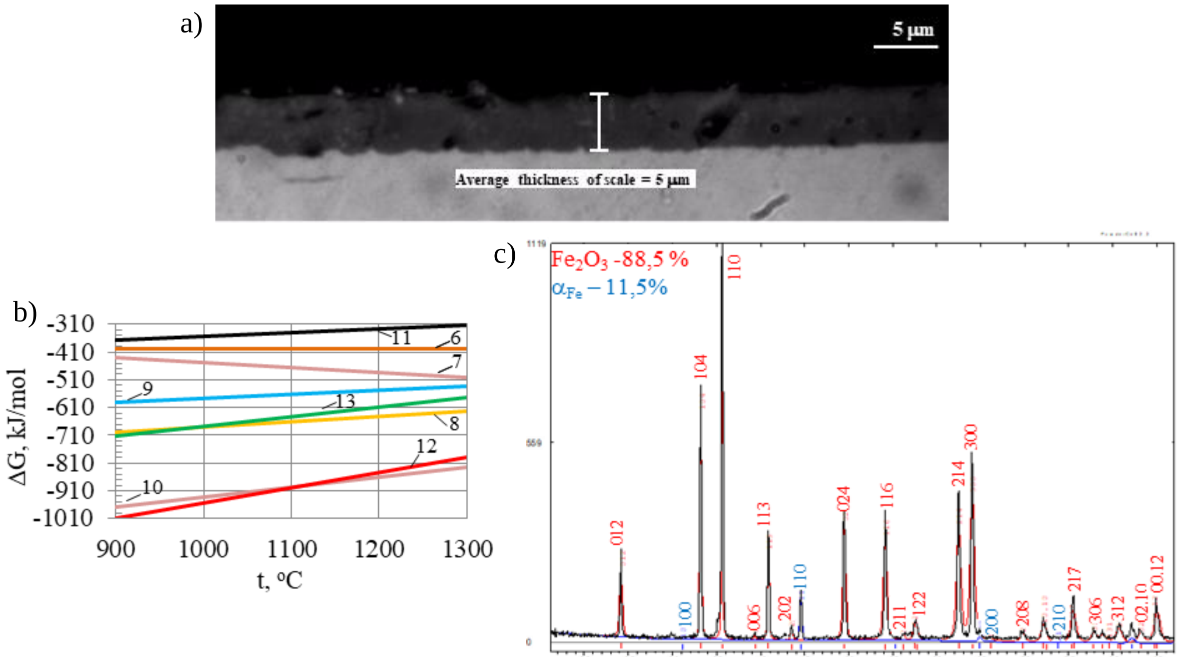


Fig. 1. **Scale on the surface of 40L steel (a), change in Gibbs free energy of oxide formation (b) and diffraction pattern of the surface of 40L steel after heating to 1000 °C (c)**

The numbers in Fig. (c) are the indices of the atomic planes of the crystal lattice. The theoretical profile of Fe_2O_3 phase is shown in red and the experimental profile in black. The experimental alpha iron profile is shown in blue.

The analysis of Gibbs free energy showed that in the temperature range from 900 to 1300 °C on the surface of carbon steels, oxidation of carbon, silicon, manganese and iron is possible according to the following reactions:

$$C + O_2 = CO_2 \uparrow, \tag{6}$$

$$2C + O_2 = 2CO \uparrow, \tag{7}$$

$$Si + O_2 = SiO_2, \tag{8}$$

$$2Mn + O_2 = 2MnO, \tag{9}$$

$$3Mn + 2O_2 = Mn_3O_4, \tag{10}$$

$$2Fe + O_2 = 2FeO, \tag{11}$$

$$4Fe + 3O_2 = 2Fe_2O_3, \tag{12}$$

$$3Fe + 2O_2 = Fe_3O_4. \tag{13}$$

The calculation results are shown in Fig. 1 b. The numbers of the lines correspond to the reaction numbers. The thermodynamic calculations showed that at 1100 °C the most probable reaction is oxidation of Fe to Fe_2O_3 oxide (Fig. 1 b). The X-ray diffraction analysis showed that under the studied conditions, a phase of 88.5% Fe_2O_3 and 11.5% Fe_α is formed on the surface of carbon steels (Fig. 1 c).

Mathematical processing of the experimental results showed that SiO_2 and K_2ZrF_6 additives influence the spreading area (S) of $Na_2B_4O_7 – B_2O_3$ system flux according to the following formulas

$$S_{SiO2} = 36.148 + 0.081 \cdot (SiO_2)^3 - 0.985 \cdot (SiO_2)^2 + 3.254 \cdot (SiO_2);\ R = 0.973, \tag{14}$$

$$S_{K2ZrF6} = 36.267 + 0.106 \cdot (K_2ZrF_6)^3 - 1.429 \cdot (K_2ZrF_6)^2 + 5.761 \cdot (K_2ZrF_6);\ R = 0.987, \tag{15}$$

The study of SiO_2 and K_2ZrF_6 additive influence on the spreading area of $Na_2B_4O_7 – B_2O_3$ system flux showed that at a temperature of 1100 °C there is an increase in the surface wettability when adding 3% SiO_2 and K_2ZrF_6 9 and 20%, respectively (Fig. 2 a). As a consequence the adhesion work of flux increases and intensifies the process of interaction of flux components with the base.

Figure 2 b. shows the change in the carbon content on the surface of high-carbon steel (1.33%C) at holding from 2 to 10 min at temperatures 800 and 1000 ºC under synthetic fluxes of the $Na_2B_4O_7 – B_2O_3$ system (lines 1, 2) and $Na_2B_4O_7 – B_2O_3$ + 3% K_2ZrF_6 + 3% SiO_2 system (lines 3, 4).

Quantitative patterns of change of the carbon content on the surface of high-carbon steel at holding (τ) from 2 to 10 min for temperature of 800 °C without additives ($C_{800(0)}$) in flux

$$C_{800(0)} = 1.33 - 0.0231 \cdot \tau;\ R = 0.999. \tag{16}$$

For temperature of 1000 °C without additives

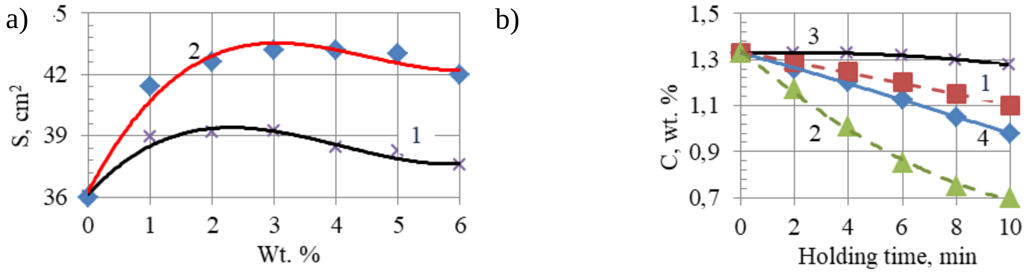
$$C_{1000(0)} = 1.34 - 0.101 \cdot \tau + 0.0035 \cdot \tau^2;\ R = 0.998. \tag{17}$$

In case of additives

$$C_{800(K2ZrF6\ +\ SiO2)} = 1.33 - 0.002 \cdot \tau - 0.0005 \cdot \tau^2 - 2 \cdot 10^{-5} \cdot \tau^3;\ R = 0.999, \tag{18}$$

$$C_{1000(K2ZrF6\ +\ SiO2)} = 1.33 - 0.031 \cdot \tau - 0.0006 \cdot \tau^2 - 2 \cdot 10^{-5} \cdot \tau^3;\ R = 0.999. \tag{19}$$

It can be seen that at 800 ºC decarburization of steel under $Na_2B_4O_7 – B_2O_3$ flux occurs at the average rate of 0.023%C per min, and at 1000 ºC – 0.063%C per min. The addition of 3% K_2ZrF_6 and 3% SiO_2 to the flux reduces the average decarburization rate at 800 ºC to 0.01%C per min, and at 1000 ºC to 0.04%C per min, i.e., 57 and 37%, respectively.



1 – SiO_2, 2 – K_2ZrF_6

1, 2 – without additives; 3, 4 – with additions of 3% K_2ZrF_6 and 3% SiO_2;
1, 3 – holding temperature 800 °C; 2, 4 –1000 ºC.
The base is a flux containing 70% $Na_2B_4O_7$ and 30% B_2O_3

Fig. 2. **Influence of K_2ZrF_6 a nd SiO_2 additives to flux of the $Na_2B_4O_7$ – B_2O_3 system on the spreading area (a) and decarburization (b) of carbon steel containing 1.33% C**

The decrease in the steel decarburization rate at adding 3% K_2ZrF_6 and 3% SiO_2 to the flux is accompanied by a decreasing of the average decarburized layer depth from 610 to 320 μm (Fig. 3a, b) .

The base is a flux containing 70% $Na_2B_4O_7$ and 30% B_2O_3

Fig. 3. **Influence of 3% K_2ZrF_6 and 3% SiO_2 additives to flux on the depth of the decarburized layer of 40L steel after holding at 1000 °C during 2 minutes**

At the same time a complete recovery of iron from scale on the steel surface is observed (Fig. 4 b), which in the case of the $Na_2B_4O_7$ – B_2O_3 system approaches 30-40% only (Fig. 4 a).

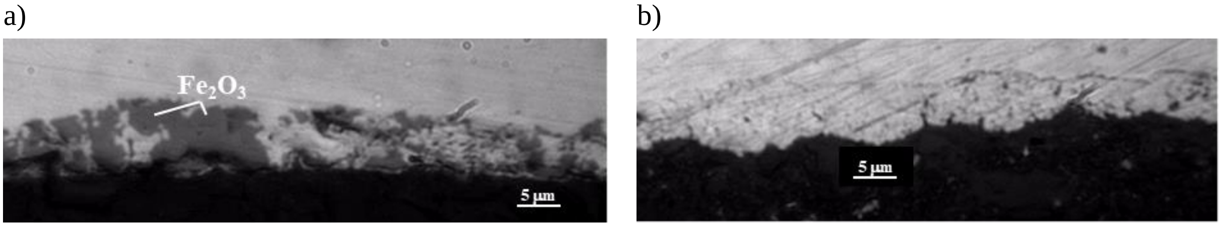


Fig. 4. **Micrographs of 40L steel surface after usage of $Na_2B_4O_7$ – B_2O_3 (a) and $Na_2B_4O_7$ – B_2O_3 – K_2ZrF_6 – SiO_2 (b) fluxes**

The influence of K_2ZrF_6 and SiO_2 additives can be explained as follows. When the flux contacts the hot metal surface it interacts with the surface elements and scale oxides.

According to the interaction of Na with K_2ZrF_6 compound, free zirconium is formed according to the following reaction [18]

$$K_2ZrF_6 + 4Na = Zr + 2KF + 4NaF. \quad (20)$$

Its formation is also possible as a result of K_2ZrF_6 dissociation in the temperature range from 238 to 576 °C [19].

The comparison of the free energies of the reactions of interaction of carbon with oxygen (6, 7) and zirconium (21) shows that the interaction of oxygen with zirconium is most probable (Figure 1 b, 5).

$$Zr + O_2 = ZrO_2, \quad (21)$$

The values of the free energy of formation of ZrO_2 (reaction 21) in the temperature range from 900 to 1300 ºC are in 2-1.6 times less for CO (reaction 7) and in 2.2-2.0 times less than for CO_2 (reaction 6), respectively. This predetermines decreasing intensity of the interaction of oxygen with carbon in the presence of zirconium and, as a consequence, decreasing the surface oxidation and decarbonization of the base when it is heated due to contact with the working layer melt.

The thermodynamic analysis of the interaction of the flux, containing K_2ZrF_6 and SiO_2, with iron oxides showed that their removal from steel surface is resulted both by the formation of $FeSiO_3$ compound (reaction 22) and its assimilation by the flux. The last happened due to the reduction of iron from oxides with Na (reaction 1) and Zr (reaction 23) (Fig. 5).

$$2\,Fe_2O_3 + 4SiO_2 = 4FeSiO_3 + O_2, \quad (22)$$

$$2Fe_2O_3 + 3Zr = 4Fe + 3ZrO_2\,, \quad (23)$$

It should be noted that the values of the free energy of reduction of Fe from Fe_2O_3 with zirconium (reaction 23) are in 3.9-14.3 times less than with carbon (reactions 4, 5) (Fig. 5), which makes a certain contribution to reducing surface decarbonization of the steel base at the manufacture of bimetallic castings. The connecting lines in Fig. 5 were obtained by constructing linear graphs based on the difference between the sum of the Gibbs free energies of the reaction products and the initial substances.

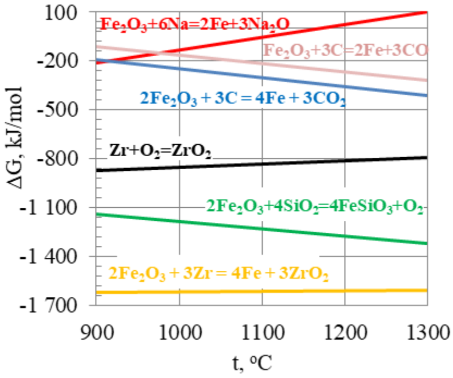


Fig. 5. **Temperature influence of free energy on interaction of $Na_2B_4O_7 – B_2O_3 – K_2ZrF_6 – SiO_2$ flux with Fe_2O_3 and oxygen**

.The study shows that fluxes containing from 60 to 80% $Na_2B_4O_7$, 10-30% B_2O_3, 3-4% K_2ZrF_6 and 3-4% SiO_2 can be effectively used as protective refining coatings that prevent metal from oxidation and reduce iron from slag formation.

Conclusions

It was established that for bimetallic casting manufacturing it is most rational to use fluxes based on $Na_2B_4O_7$ and B_2O_3. The main requirements for protective coatings are high wettability and work of adhesion to the surface of the solid base and high refining capacity for oxides.

It was found that addition to the flux of 3 to 4% K_2ZrF_6 and SiO_2 increases the wettability of the surface 9 and 20% and reduces the average rate of decarburization in the temperature range from 800 to 1000 °C 57 and 37%. In this case, complete reduction of iron from scale on the steel surface is observed, which in the case of the $Na_2B_4O_7 – B_2O_3$ system is 30-40% only.

The mechanism was proposed for the influence of the additions of K_2ZrF_6 and SiO_2 on the properties of the $Na_2B_4O_7 – B_2O_3$ system flux, which consists in the prevailing effect of zirconium on protecting the surface of the steel base from oxidation and decarburization.

The following optimal flux composition is recommended (wt.%): $Na_2B_4O_7$ – from 60 to 80; B_2O_3 – from 10 to 30;% K_2ZrF_6 – from 3 to 4%; SiO_2 from 3 to 4%. This application could improve the production of steel based bimetallic castings and increase their properties.

Author contributions

Conceptualization, Y.A.; methodology, Y.A. and S.G.; experimentation, S.G. and H.M.; results analysing, Y.A., S.G., H.M., V.K. and V.L.; formal analysis, Y.A. and S.G.; writing – original draft preparation, Y.A. and S.G.; writing – review and editing, S.G., H.M., V.K. and V.L. All authors have read and agreed to the published version of the manuscript.

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