Use of barium-strontium carbonate for flux welding and surfacing of mining machines

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Abstract. The results of application of barium-strontium carbonate for modifying and refining iron-carbon alloys, used for welding and surfacing in ore mining and smelting industry, are generalized. The technology of manufacturing a flux additive containing 70% of barium-strontium carbonate and 30% of liquid glass is proposed. Several compositions of welding fluxes based on silicomanganese slag were tested. The flux additive was introduced in an amount of 1, 3, 5%. Technological features of welding with the application of the examined fluxes are determined. X-ray spectral analysis of the chemical composition of examined fluxes, slag crusts and weld metal was carried out, as well as metallographic investigations of welded joints. The principal possibility of applying barium-strontium carbonate as a refining and gas-protective additive for welding fluxes is shown. The use of barium-strontium carbonate reduces the contamination of the weld seam with nonmetallic inclusions: non-deforming silicates, spot oxides and brittle silicates, and increases the desulfurizing capacity of welding fluxes.

1. Introduction
The issues of development of new flux compositions and the use of relatively inexpensive natural materials in the form of additives to welding fluxes that allow purposefully the physical and chemical state of the metal melt to be controlled in order to improve the qualitative characteristics of the weld are paid much attention both in Russia and abroad [1-12]. In metallurgy one of the promising areas is the development of technologies that allow steel with barium and strontium from oxide materials to be modified and refined skipping the stages of ligature production [13-15].

As a material for such technologies the most promising one is the deposit of complex carbonate ores containing calcium, barium and strontium in the northeast of Irkutsk region. The ores have the following mineral composition: 70-80% strontium-calcium-barium carbonate, 10% potassium feldspar, 10-20% pyroxene. The production of barium-strontium modifier BSK-2 according to TU 1717-001-75073896–2005 was developed by “NPK Metalltekhnoprom” OJSC. The modifier is intended for the production of steel, cast iron and non-ferrous alloys, as well as for welding electrode coatings [16-19]. The barium-strontium modifier contains 13.0-19.0% BaO, 3.5 – 7.5% SrO, 17.5 – 25.5% CaO, 19.8 – 29.8% SiO2, 0.7 – 1.1% MgO, 2.5 – 3.5% K2O, 1.0 – 2.0% Na2O, 1.5 – 6.5% Fe2O3, 0 – 0.4% MnO, 1.9 – 3.9% Al2O3, 0.7 – 1.1% TiO2, 16.0-20.0% CO2.

The results of X-ray phase analysis [19] showed that the main compounds that make up the barium-strontium modifier are BaCaO (CO3)2, calcite CaCO3, calciostrontianite CaSr(CO3)2, dolomite MgCO3 and siderite FeCO3. The differential-thermal analysis determined that up to 1223 K the dissociation of dolomite, calcite, baritocalcite and calciostrontianite occurs. This means that at temperatures of
welding processes (1873-1923 K) it is possible to use this material with the decomposition of carbonate constituents at a temperature of 1273 K according to the reactions [13]:

\[
\begin{align*}
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2↑, \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2↑, \\
\text{BaCa}(\text{CO}_3)_2 & \rightarrow \text{BaCO}_3 + \text{CaO} + \text{CO}_2↑, \\
\text{CaSr}(\text{CO}_3)_2 & \rightarrow \text{SrCO}_3 + \text{CaO} + \text{CO}_2↑
\end{align*}
\]

with the subsequent dissociation of barium and strontium carbonates according to the reactions:

\[
\begin{align*}
\text{BaCO}_3 & \xrightarrow{1273K} \text{BaO} + \text{CO}_2↑, \\
\text{SrCO}_3 & \xrightarrow{1373K} \text{SrO} + \text{CO}_2↑.
\end{align*}
\]

In [20, 21] to determine the conditions for the reduction of barium and strontium from oxides thermodynamic modeling methods implemented in the Terra software complex were used.

Based on the study of decomposition kinetics of barytocalcite and calciostrontianite the authors in believe [22, 23] that the process proceeds in two stages, as a result of which CaO, BaO, and SrO are formed and carbon dioxide (CO\(_2\)) is released. The release of CO\(_2\) during barium and strontium carbonates dissociation creates a protective atmosphere for the welded products, thereby protecting the molten metal from oxidation and improving the quality of the weld. At the same time the protection is due to high-temperature decomposition of carbonates with the formation of CO\(_2\).

Calculations [24, 25] show that during decomposition of 1 kg of CaCO\(_3\) (n.c.) 0.224 m\(^3\) of CO\(_2\) is formed, 1 kg of MgCO\(_3\) – 0.267 m\(^3\), 1 kg of FeCO\(_3\) – 0.192 m\(^3\), 1 kg of MnCO\(_3\) – 0.194 m\(^3\), 1 kg of Na\(_2\)CO\(_3\) – 0.211 m\(^3\). Accordingly, with the decomposition of 1 kg of BaCO\(_3\) (n.c.), 0.114 m\(^3\) of CO\(_2\) is formed, 1 kg of SrCO\(_3\) – 0.152 m\(^3\) of CO\(_2\). When heated to the temperature of welding processes 1800 °C (2073 K) the gas expansion in 7.6 times takes place. Apparently, without taking into account the costs of carbonates decomposition, the most optimal is the use of MgCO\(_3\), CaCO\(_3\), BaCa (CO\(_3\))\(_2\) and CaSr(CO\(_3\))\(_2\) as components that make it possible to obtain the greatest amount of CO\(_2\) during decomposition of 1 kg of material.

The carbonates dissociation contained in barium-strontium carbonatite (MgO, CaO, BaO, SrO) increases the basicity of slag and, apparently, contributes to the refining of the weld metal from nonmetallic inclusions. It is believed that barium and strontium, being modifiers, affect the metallic structure of the welded joint [19].

In [26] it is shown that it is possible to use carbonatite as an additive to welding fluxes. Further studies concerning the effect of the additive of barium-strontium carbonatite, when introduced into welding fluxes, on the quality of obtained welds are given in this paper.

2. Methods of research

In a series of experiments performed in the laboratory conditions various compositions of welding fluxes were prepared and investigated.

Welding flux No. 1 (flux additive) was made by mixing barium-strontium carbonatite with liquid glass in a ratio of 70% and 30%, respectively. After exposure at room temperature it was dried in an oven at a temperature of 300 °C, then cooled, crushed and sieved with fractionation 0.45-2.5 mm. Flux No. 2 – flux based on silicomanganese slag of fraction 0.45-2.5 mm, fluxes No. 3, 4, 5 – silicomanganese slag of fraction 0.45-2.5 mm mixed with flux additive (barium-strontium carbonatite with liquid glass in a ratio of 70% to 30%) in amounts of 1; 3 and 5%, respectively.

Butt welding was performed without a double bevel on samples with measures 500×75 mm, thickness 16 mm, from sheet steel 09G2S. The process was carried out using a S-08GA wire with a diameter 4 mm by ASAW-1250 welding tractor in the following modes: I = 700 A; U = 30 V; V = 35 m/h.
3. Results and research
Chemical compositions of fluxes, slag crusts and weld metal are given in tables 1, 2 and 3. As it can be seen from the tables there is an insignificant recovery of barium and strontium from the material, and a change in the chemical composition of the weld indicates an increase in the degree of desulfurization with the use of a flux additive.

Table 1. Chemical composition of flux, %.

| Sample No. | MnO | SiO₂ | CaO | MgO | Al₂O₃ | FeO | Na₂O | K₂O | BaO | SrO | S | P |
|------------|-----|------|-----|-----|-------|-----|------|-----|-----|-----|---|---|
| 1          | 0.87 | 32.52 | 12.15 | 1.02 | 3.54  | 9.96 | -    | 2.41 | 2.48 | 14.24 | 4.86 | 0.25 | 0.21 |
| 2          | 9.58 | 50.26 | 18.51 | 7.98 | 10.55 | 1.54 | 0.38 | 0.41 | 0.61 | orc.  | orc. | 0.13 | 0.05 |
| 3          | 8.11 | 47.64 | 29.79 | 6.19 | 6.97  | 0.31 | 0.21 | 0.27 | orc.  | 0.25  | 0.10 | 0.15 | 0.01 |
| 4          | 7.96 | 48.28 | 28.36 | 6.15 | 7.05  | 0.42 | 0.33 | 0.43 | 0.03  | 0.61  | 0.21 | 0.15 | 0.02 |
| 5          | 8.19 | 48.44 | 28.86 | 5.08 | 7.04  | 0.54 | 0.31 | 0.43 | 0.04  | 0.65  | 0.25 | 0.15 | 0.02 |

Table 2. Chemical composition of slag crusts.

| Sample No. | FeO | MnO | SiO₂ | Al₂O₃ | MgO | Na₂O | K₂O | BaO | SrO | F | S | P |
|------------|-----|-----|------|-------|-----|------|-----|-----|-----|---|---|---|
| 1          | 2.42 | 4.92 | 18.81 | 26.21 | 14.84 | 18.11 | 0.70 | 0.38 | 0.51 | 0.10 | - | 0.15 | 0.04 |
| 2          | 2.11 | 8.05 | 23.83 | 46.92 | 10.27 | 6.90 | 0.38 | 0.66 | orc.  | orc.  | 0.74 | 0.13 | 0.01 |
| 3          | 1.76 | 8.21 | 29.34 | 46.74 | 7.17  | 5.79 | 0.28 | orc.  | 0.25  | 0.10 | 0.23 | 0.15 | 0.01 |
| 4          | 2.45 | 8.42 | 27.36 | 46.94 | 6.92  | 6.90 | 0.39 | 0.04 | 0.59  | 0.24  | 0.27 | 0.15 | 0.02 |
| 5          | 2.70 | 7.93 | 27.36 | 46.94 | 6.87  | 5.94 | 0.47 | 0.12 | 0.90  | 0.32  | 0.32 | 0.15 | 0.02 |

Table 3. Chemical composition of welded joints.

| Sample No. | C    | Si   | Mn   | Cr   | Ni   | Cu   | Nb   | Al   | S    | P    | Sr  | Ba  |
|------------|------|------|------|------|------|------|------|------|------|------|-----|-----|
| 1          | 0.11 | 0.13 | 0.53 | 0.02 | 0.05 | 0.10 | 0.002 | -    | 0.030 | 0.021 | 0.0004 | 0.004 |
| 2          | 0.09 | 0.71 | 1.51 | 0.03 | 0.10 | 0.11 | 0.014 | 0.023 | 0.019 | 0.013 | orc.  | orc. |
| 3          | 0.08 | 0.54 | 1.38 | 0.02 | 0.04 | 0.06 | 0.016 | 0.012 | 0.011 | 0.009 | 0.0004 | 0.0012 |
| 4          | 0.08 | 0.51 | 1.33 | 0.02 | 0.03 | 0.06 | 0.015 | 0.021 | 0.010 | 0.008 | 0.0004 | 0.0021 |
| 5          | 0.09 | 0.57 | 1.41 | 0.02 | 0.03 | 0.04 | 0.020 | 0.020 | 0.008 | 0.009 | 0.0004 | 0.0033 |

Visual quality control of the welded joints of samples No. 1, prepared with the use of flux additives only, showed unsatisfactory quality – uneven shape of the seam, with poor separation of the slag crust. The remaining samples are of satisfactory quality.

Samples were cut from the welded plates and X-ray spectral analysis of the weld metal composition, metallographic examinations of the weld metal were performed, the mechanical properties were identified – they are given in table 5. In connection with the unsatisfactory quality of the welded bead on sample No. 1 no mechanical properties were determined.

The metallographic study was carried out on polished sections without etching with OLYMPUS GX-51 optical microscope with magnification × 100. The results of the analysis for the presence of nonmetallic inclusions in the weld zone, carried out in accordance with GOST 1778-70, are shown in figure 1 and table 4. The points of nonmetallic inclusions were established when examining the entire area of welded seams of non-etched polished sections. In each field of vision the dimensions were determined separately for each type of nonmetallic inclusions by comparison with reference scales.

Studies indicate a reduction in the contamination of the weld metal by non-deforming silicates and the absence of brittle silicates.

The microstructure was studied with OLYMPUSGX-51 optical microscope in a bright field in the magnification range × 500 after etching the sample surface in a 4% nitric acid solution. The grain size was determined according to GOST 5639-82 at magnification × 100. The microstructures of the weld
metal are shown in figure 2. The weld metal is characterized by the formation of a ferrite-perlite structure of vismanthtiten orientation. In this case in the samples containing strontium and barium a slight decrease in the grain size is observed. The grain size in the welded sample with a flux that does not contain barium-strontium carbonatite is No. 4 on the grain scale, and the grain size in the welded samples (No. 3, No. 4, No. 5) with the flux containing barium-strontium carbonatite is No. 4, No. 5.

![Figure 1](image1)

**Figure 1.** Non-metallic inclusions in the weld zone of samples: a) sample 3; b) sample 4; c) sample 5; d) sample 6.

| Sample No. | Non-metallic inclusions, point | Non-deforming silicates | Brittle silicates | Spit oxides |
|------------|--------------------------------|-------------------------|-------------------|-------------|
| 3          | 4b; 3b; 4a                     | 3b                      | 1a                |
| 4          | 4b; 3a                         | -                       | 1a; 2a            |
| 5          | 4b; 2b; 2a                     | -                       | 1a; 2a            |
| 6          | 4b; 3a; 4a                     | -                       | 1a; 2a; 3a        |

![Figure 2](image2)

**Figure 2.** Welded joints microstructure of samples with the addition of barium-strontium carbonatite, %: a) 0; b) 1; c) 3; d) 5.

Samples were cut from the welded plates and mechanical properties were determined. As a result of studying the mechanical properties of samples cut from welded plates results were obtained indicating an increase in the values of the impact hardness and and yield stress (figure 3, 4).

![Figure 3](image3)

**Figure 3.** Influence of the content of barium-strontium carbonatite in the flux on impact hardness.
4. Conclusions
1. The principal possibility of using barium-strontium carbonatite as a refining and gas-protective additive for welding fluxes is shown.
2. The use of barium-strontium carbonatite allows contamination of the weld seam with nonmetallic inclusions (non-deforming silicates, spot oxides and brittle silicates) to be reduced and the desulfurizing capacity of welding fluxes to be increased.
3. Introduction of barium-strontium carbonatite in the amount of 5% into the flux from silicomanganese slag forms a ferrite-perlite structure of the weld metal of vismanthtiten orientation, while the grain size from No. 4 to No. 4, No. 5 is slightly reduced.
4. The impact hardness and yield stress of the samples are increased by introduction of barium-strontium carbonatite into the flux composition.

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