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### ARTICLE

# Using barium-strontium carbonatite in submerged-arc welding

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#### ABSTRACT

It is shown that the barium–strontium carbonatite can be used as a refining and gas-shielding addition for welding fluxes.Welding with the barium–strontium carbonatite reduces the degree of contamination of the welded joint with non-metallic inclusions: non-deformed silicates, spot oxides in brittle silicates, and also increases the desulfurization capacity of the welding fluxes. The addition of the barium–strontium carbonatite to the flux based on the slag of silicomanganese in the amount of up to 5% results in the formation of a ferritic–pearlitic structure of the metal of the welded joint with the Widmanstätten direction, with a small decrease of the grain size. The impact toughness and yield strength of the specimens increase as a result of adding the barium–strontium carbonatite to the flux, and the ductility properties and ultimate tensile strength of the samples decrease.

#### **KEYWORDS**

welding; fluxes; technology; welding joint; bariumstrontium carbonatite; samples; nonmetallic inclusions; microstructure; grain size; mechanical properties

The problems of development of new compositions of fluxes and the application of relatively cheap natural materials in the form of additions to welding fluxes for controlling in the required direction the physical-chemical state of the metallic melt in order to increase the quality parameters of the welded joint have been studied extensively both in the Russian Federation and abroad [1-12]. At the same time, one of the promising directions in metallurgy is the development of a technology of modification and refining of steel with barium and strontium using oxide materials, bypassing the stage of production of master alloys [13-15]. The materials for these technologies represent mostly the deposits of complex carbonate ores, containing calcium, barium and strontium in the North East of the Irkutsk region. The ores have the following mineral composition: 70-80% of the strontium-calcium-barium carbonate, 10% of potassium fluorspar, 10-20% of pyroxene. The modification agent is designed for the production of steel, cast iron and non-ferrous alloys and also for the coatings of welding electrodes [16-19]. The barium - strontium modification agent includes: 13.0-19.0% BaO, 3.5-7.5% SrO, 17.5-25.5% CaO, 19.8-29.8% SiO<sub>2</sub>, 0.7-1.1% MgO, 2.5-3.5% K<sub>2</sub>O, 1.0-2.0% Na<sub>2</sub>O, 1.5-6.5% Fe<sub>2</sub>O<sub>3</sub>, 0-0.4% MnO, 1.9-3.9% Al<sub>2</sub>O<sub>3</sub>, 0.7-1.1% TiO<sub>2</sub>, 16.0-20.0% CO<sub>2</sub>.

The results of x-ray diffraction analysis show [19] that the main compounds, included in the composition of the barium–strontium modification agent are barytocalcite BaCa(CO<sub>3</sub>)<sub>2</sub>, calcite CaCO<sub>3</sub>, calcium strontianite CaSr(CO<sub>3</sub>)2, dolomite MgCO<sub>3</sub> and siderite FeCO<sub>3</sub>. The results of differential thermal analysis indicate that temperatures up to 1223 K result in

the dissociation of dolomite, calcite, barytocalcite and calcium strontianite. This means that in welding at the temperatures of 1873–1923 K it is possible to use this material with the dissociation of carbonate components at a temperature of 1273 K by the reaction [13]

$$MgCO_3 \rightarrow MgO + CO_2 \uparrow$$
 (1)

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$
 (2)

$$BaCa(CO_3)_2 \rightarrow BaCO_3 + CaO + CO_2 \uparrow$$
 (3)

$$CaSr(CO_3)_2 \rightarrow SrCO_3 + CaO + CO_2 \uparrow$$
 (4)

with subsequent dissociation of the barium and strontium carbonates by the reaction

$$BaCO_3 \xrightarrow{>1273 K} BaO + CO_2 \uparrow$$
 (5)

$$SrCO_3 \xrightarrow{>1373 K} SrO + CO_2 \uparrow$$
 (6)

In the investigations described in [20,21] the conditions of reduction of barium and strontium from the oxides were determined using the methods of thermodynamic simulation, realized in the Terra software.

In the investigation of the kinetics of dissociation of the barytocalcite and calcium strontianite it is assumed in [2,5] that the process takes place in two stages resulting in the formation of CaO, BaO, SrO and generation of carbon dioxide (CO<sub>2</sub>). The generation of CO<sub>2</sub> in the dissociation of the barium and strontium carbonates produces a shielding atmosphere for the welded components and, consequently, it protects the molten metal



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against oxidation and increases the quality of the welded joint. Shielding is carried out as a result of the high-temperature dissociation of the carbonates with the formation of CO<sub>2</sub>. The calculations carried out in [22,23] showed that the dissociation of 1 kg of CaCO<sub>3</sub> (specific weight) results in the formation of 0.224 m<sup>3</sup>  $CO_2$ , 1 kg Mg $CO_3$  – 0.194 m<sup>3</sup>, 1 kg Na<sub>2</sub> $CO_3$  – 0.211 m<sup>3</sup>. Correspondingly, the dissociation of 1 kg of BaCO<sub>3</sub> (specific weight) results in the formation of 0.114 m<sup>3</sup> of CO<sub>2</sub>, 1 kg SrCO<sub>3</sub> - 0.152 m<sup>3</sup> CO<sub>2</sub>. Heating to the temperature of the welding processes 1800°C (2073 K) is accompanied by the expansion of the gas by a factor of 7.6. Evidently, without taking into account the losses caused by the dissociation of the carbonates, the optimum procedure is the application of MgCO<sub>3</sub>, CaCO<sub>3</sub>,  $BaCa(CO_3)_2$  and  $CaSr(CO_3)_2$  as the components producing the largest amount of CO<sub>2</sub> in dissociation of 1 kg of material.

The dissociation of the carbonates, present in the barium–strontium carbonatite (MgO, CaO, BaO, SrO) increases the basicity of the slag and, evidently, supports the removal of non-metallic inclusions from the metal of the welded joint. It is assumed that in addition to this process, barium and strontium, being modification agents, influence the metallic structure of the welded joint [19].

The results obtained in [24] show that the bariumstrontium carbonatite can be used as an addition to welding fluxes. Further investigations of the effect of the addition of the barium-strontium carbonatite added to the welding fluxes and its effect on the quality of the produce welded joints are presented in this article. The experiments carried out in the laboratory conditions were conducted using different compositions of welding fluxes.

The welding flux No. 1 (flux-addition) was produced by mixing the barium–strontium carbonatite with water glass at a ratio of 70 and 30%, respectively. This was followed by holding at room temperature and then by drying in a furnace at a temperature of  $300^{\circ}$ C, cooling, crushing and screening with the separation of the 0.45–2.5 mm fraction. Flux No. 2 was based on the slag produced in the production of silicomanganese with the fraction of 0.45–2.5 mm, fluxes Nos. 3, 4, 5 – the slags produced in the production of silicomanganese with the flux-addition (the barium–strontium carbonatite with the water glass at a ratio of 70% and 30%) in the amounts of 1, 3 and 5%, respectively.

Submerged-arc welding was carried out by butt welding without edge preparation on two sides on specimens  $500 \times 75$  mm in size, thickness 16 mm, in sheets of 09G2S steel. Welding was conducted using Sv-08GA wire, with a diameter of 4 mm, using ASAW-1250 welding equipment in the conditions:  $I_w = 700$  A,  $U_a = 30$  V,  $V_w = 35$  m/h.

The chemical composition of the fluxes, the slag crust and the metal of the welded joints are presented in Tables 1–3, respectively. As indicated by the Tables, barium and strontium are reduced only slightly from the material, and the variation of the chemical composition of the welded joint indicates the increase of the degree of desulfurization when using the flux-addition.

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		Mass fraction of elements, % (in flux composition)											
Specimen No.	MnO	SiO2	CaO	MgO	$AI_2O_3$	FeO	F	Na <sub>2</sub> O	K <sub>2</sub> O	BaO	SrO	S	Р
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	отс.	OTC.	0,13	0,05
3	8,11	47,64	29,79	6,19	6,97	0,31	0,21	0,27	отс.	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	0,21 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

Та	b	le	2.

		Mass fraction of elements, % (in slag crust composition)											
Specimen No.	FeO	MnO	CaO	SiO <sub>2</sub>	$AI_2O_3$	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	BaO	SrO	F	S	Р
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	OTC.	OTC.	0,74	0,13	0,01
3	1,76	8,21	29,34	46,74	7,17	5,79	0,28	OTC.	0,25	0,10	0,23	0,15	0,01
4	2,45	8,42	27,66	46,90	6,92	6,00	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.

		Mass fraction of elements, % (in metal of welded joint)											
Specimen No.	С	Si	Mn	Cr	Ni	Cu	Nb	Al	S	Р	Sr	Ва	
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	отс.	отс.	
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	



**Figure 1.** Non-metallic inclusions in the welding zone of the specimens: a) specimen 3; b) specimen 4; c) specimen 5; d) specimen 6. mkm =  $\mu$ m.

Table /

Visual inspection of the quality of the welded joint in the specimen No. 1, produced using only the fluxaddition showed that the quality is not satisfactory – the shape of the welded joint is non-uniform, with poor separation of the slag crust. The quality of the remaining specimens was satisfactory.

Non-metallic inclusions, grain size scale No.								
Non-deformed silicates	Brittle silicates	Spot oxides						
4b; 3b; 4a	3b	1a						
4b; 3a	OTC.	1a; 2a						
4b; 2b; 2a	OTC.	1a; 2a						
4b; 3a; 4a	OTC.	1a; 2a; 3a						
	Non-metallic inclus Non-deformed silicates 4b; 3b; 4a 4b; 3a 4b; 2b; 2a 4b; 2a 4b; 3a; 4a	Non-metallic inclusions, grain size sNon-deformed silicatesBrittle silicates4b; 3b; 4a3b4b; 3aott.4b; 2b; 2aott.4b; 3a; 4aott.						



**Figure 2.** The microstructure of welded joints in the specimens with the addition of barium–strontium carbonatite, %; a) 0; b) 1; c) 3; d) 5. mkm =  $\mu$ m.



**Figure 3.** The effect of the content of the barium–strontium carbonatite in the flux on the impact toughness values. Содержание барийстронцевого карбинита во флюсе, % = Barium–strontium carbonatite content of the flux, %; Ударная вязкость при  $T = +20^{\circ}$ С, Дж/см<sup>2</sup> = Impact toughness at  $T = +20^{\circ}$ С, J/сm<sup>2</sup>.

The welded sheets were machined to produce specimens for x-ray spectrum analysis of the composition of the metal of the welded joints, metallographic studies of the metal of the welded joints and the determination of the mechanical properties. Because of the unsatisfactory quality of the weld bead produced on the specimen No. 1, this sample was not used for the determination of the mechanical properties. Metallographic studies were carried out on microsections without etching using an Olympus GX-51 optical microscope at a magnification of  $\times 100$ . The results of analysis to determine the presence of non-metallic inclusions in the zone of the welded joint, carried out in accordance with the GOST 1778–70 standard, are presented in Figure 1 and Table 4. The grain size of the nonmetallic inclusions was determined by examination of the entire area of the welded joints on the unetched sections.



Figure 4. Effect of the content of the barium–strontium carbonatite in the flux on yield strength. Содержание барийстронцевого карбинита во флюсе, % = Barium–strontium carbonatite content of the flux, %; Предел текучести,  $\sigma_T$ , H/мм<sup>2</sup> = Yield strength  $\sigma_T$ , N/mm<sup>2</sup>.

The size of each type of the non-metallic inclusion were determined in each field of the specimen by comparing with the standard scale.

The experimental results indicate a decrease of the degree of contamination of the metal of the welded joint with non-deformed silicates and the absence of brittle silicates.

The microstructure was studied in the Olympus GX-51 optical microscope in the bright field at a magnification of ×500 after etching the surface of the specimens in a 4% solution of nitric acid. The grain size was determined in accordance with the GOST 5630-82 standard, at a magnification of ×100. The microstructures of the metal of the welded joints are shown in Figure 2. The metal of the welded joint was characterized by the formation of the structure of ferrite - pearlite with the Widmanstätten morphology. The specimens containing strontium and barium were characterized by a small decrease of the grain size. The grain size in the specimen welded under the flux without the barium-strontium carbonatite was equal to No. 4 on the grain size scale, and the grain size of the specimens (Nos. 3, 4 and 5) welded under the flux with the addition of the barium-strontium carbonatite was No. 4 and No. 5.

The welded sheets were machined to produce specimens for the determination of the mechanical properties. The results of determination of the mechanical properties of the specimens taken from the welded sheets show the increase of the impact toughness and real strength values (Figures 3 and 4).

## Conclusions

- (1) It is shown possible to use the barium-strontium carbonatite as the refining and gasshielding addition for the welding fluxes.
- (2) The application of the barium-strontium carbonatite reduces the degree of contamination of the welded joint with non-metallic inclusions: the non-deformed silicates, spot

oxides and brittle silicates, and also increases the desulfurization capacity of the welding fluxes.

- (3) The addition of up to 5% of the barium-strontium carbonatite to the flux based on the silicomanganese slag produces the ferritic-pearlitic structure of the metal of the welded joint with the Widmanstätten morphology, resulting in a small decrease of the grain size from No. 4 to No. 4, No. 5.
- (4) The impact toughness and the yield strength of the specimens increased when the bariumstrontium carbonatite was added to the welding flux.

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