Metallurgical Properties and Phase Transformations of Barium-Strontium Modifier

M A Platonov1,a, I S Sulimova1,b, I D Rozhikhina3,c, V I Dmitrienko4,c, G V Horoshun5

1,2,5National Research Tomsk Polytechnic University, Yurga Technological Institute branch of Tomsk Polytechnic University 652050, Kemerovo region
3,4Siberian State Industrial University, Novokuznetsk, Russia

E-mail: a maxrauber@mail.ru, b siris78@mail.ru, c kafamsf@sibsiu.ru

Abstract. Metallurgical properties and phase transformations of barium-strontium modifier were tested in laboratory conditions resembling steel processing in furnace and ladle. When heating barium-strontium modifier start of melting, kinetics of decomposition, phase and structure transformation were studied. The concentrate under consideration has been revealed to be a complex mineral compound containing barytocalcite, calcite, calciostrontianite, dolomite and siderite. The reaction kinetics of decomposing mineral components of barium-strontium modifier to oxides does not considerably affect slag formation in conditions of out-of-furnace steel processing.

Introduction

Barium-strontium modifier BSC-2 is used in metallurgical production. To develop efficient technologies of its application detailed investigation into the processes taking place when introducing modifier into steel is required.

Chemical composition of barium-strontium modifier BSC-2, %: 16.0 BaO; 5.5 SrO; 21.5 CaO; 24.8 SiO2; 0.9 MgO; 3.0 K2O; 1.5 Na2O; 4.0 Fe2O3; 0.2 MnO; 2.9 Al2O3; 0.9 TiO2; 18.0 CO2 (Technical Conditions 1717-001-75073896).

The research into mineral composition of barium-strontium modifier and integrated investigations of phase transformations provide means of obtaining data on nature and special features of modifier mineral formation, as well as change in the structure of raw materials under heating.

X-ray phase analysis at temperature T = 293 K (figure 1) has revealed core compounds barium-strontium modifier consists of are barytocalcite BaCa(CO3)2, calcite CaCO3, calciostrontianite CaSr(CO3)2, dolomite MgCO3 and siderite FeCO3 impurities.

Differential thermal analysis implemented by means of thermal gravimetric method was applied to study phase and structure transformations occurring in ore mineral components of barium-strontium modifier under heating.
To whom any correspondence should be addressed.

Figure 1. Fragment of barium-strontium modifier X-ray diffraction pattern.

The sample was heated up to 1223 K at rate 10 degree a minute. Survey mode: DTA = 1/5; DTG = 1/10, Pmass = 500 mg. Table 1 presents the results of differential thermal analysis of barium-strontium modifier.

| T, K | Phase composition                           |
|------|--------------------------------------------|
| 381  | Phase transformations in impurities        |
| 568  | Phase transformations in impurities        |
| 743  | Phase transformations in impurities        |
| 913  | Phase transformations in impurities        |
| 1018 | Dolomite dissociation                      |
| 1173 | Calcite dissociation                       |
| 1223 | Barytocalcite and calciostrontianite dissociation |
Figure 2 displays results obtained in the course of differential thermal analysis of barium-strontium modifier thermogram.

Thermo gravimmetrical analysis of the modifier identified adsorbed water removal when heating up to 381 K. Further heating up to 381 – 913 K conditions phase transformations in impurities. Within temperature interval 913 – 1018 K dolomite dissociation resulting in MgO formation takes place. Further heating up to 1018 – 1223 K causes dissociation of calcite, barytocalcite, and calciostrontianite, alongside with mass loss 11.57 %.

Carried out investigations show barium-strontium modifier is a complex mineral compound containing barytocalcite, calcite, calciostrontianite, dolomite and siderite. Differential thermal analysis determined the sequence of phase transformations, arising in ore mineral components of barium-strontium modifier under heating.

Differential thermal analysis and investigations into kinetics of barium-strontium modifier decomposition (figure 4) pointed at successive reactions when heating barium-strontium modifier:

\[ \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \uparrow, \]
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow, \]

The kinetics of modifier decomposition was tested to determine the influence of barium-strontium modifier on properties of forming slag. The kinetics of decomposition was studied gravimetrically at temperatures 1673 and 1773 K according to mass decrease of 20 g modifier sample, particle dimensions 0.01 – 0.1 mm. Mass decrease was registered every minute. The layout of the appliance is shown in figure 3.

Differential thermal analysis and investigations into kinetics of barium-strontium modifier decomposition (figure 4) pointed at successive reactions when heating barium-strontium modifier:
BaCa(CO₃)₂ → BaCO₃ + CaO + CO₂↑,
CaSr(CO₃)₂ → SrCO₃ + CaO + CO₂↑,
BaCO₃ → BaO + CO₂↑, 
SrCO₃ → SrO + CO₂↑.

Figure 3. Layout of experimental appliance.

Figure 4. Dissociation kinetics of barium-strontium modifier at temperatures 1673 K (1) and 1773 K (2).

Therefore, temperature increase up to 1673 and 1773 K, reaction rate of decomposing mineral components of barium-strontium modifier to oxides do not affect slag formation in conditions of out-of-furnace steel processing.

Resistance furnace with platinum heater was used to specify the start of barium-strontium modifier melting. The layout of the furnace is displayed in figure 5.
When heating a platinum plate behavior of barium-strontium modifier placed on a hot junction was observed visually by a binocular microscope with 30 – 50 fold magnification in the reflected light.

To specify the start of melting a sample of barium-strontium modifier was grinded in the mortar so grains 0.01 – 0.1 mm were obtained, then 5 – 7 grains of matter under consideration were placed under a hot junction. The furnace heating rate up to temperature 1473 – 1573 K was 100 – 150 degree a second, then 20 – 30 degree a second, about the temperature of melting – 3 – 5 degree a second. The first attempt to determine melting temperature of barium-strontium modifier is an approximate one, used to define temperature boundaries of the experiment.

The temperature when sharp edges of barium-strontium modifier particles fuse was considered the start of melting. Starts of barium-strontium modifier melting are 1641 – 1655 K according to the results of carried out experiments represented in table 2.
Table 2. Starts of melting of barium-strontium modifier

| № experiment | Start of melting, K Barium-strontium modifier | Start of melting, K Slag mixture |
|--------------|---------------------------------------------|---------------------------------|
| 1            | 1653                                        | 1640                            |
| 2            | 1641                                        | 1645                            |
| 3            | 1655                                        | 1651                            |
| 4            | 1653                                        | 1653                            |
| 5            | 1645                                        | 1644                            |
| 6            | 1653                                        | 1655                            |
| 7            | 1653                                        | 1648                            |
| 8            | 1644                                        | 1643                            |
| 9            | 1653                                        | 1655                            |
| 10           | 1653                                        | 1642                            |

Mixture containing modifier (15 %) and lime (85 %) was melted at temperature 1873 K to find out the influence of barium-strontium modifier on properties of slag formed when processing steel in resistance furnace with coal tube heater. After the sample had been cooled down, melting temperatures of a slag mixture were tested according to the described above procedure. The results of carried out experiments demonstrated (table 2) starts of melting of a slag mixture are similar to those of barium-strontium modifier and are equal to 1640 – 1655 K.

Conclusions

The tests of material composition revealed the concentrate under consideration to be a complex mineral compound containing barytocalcite, calcite, calciostrontianite, dolomite and siderite. The reaction kinetics of decomposing mineral components of barium-strontium modifier to oxides does not considerably affect slag formation in conditions of out-of-furnace steel processing. Starts of melting are 1641 – 1655 K for barium-strontium modifier; 1640 – 1654 K for slag mixture containing the modifier (15 %) and lime (85 %).

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