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Application of Natural Barium-Stroncium Containing Material for Steel Treatment

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Abstract. The paper considers carbon, silicon and aluminum reduction of barium and strontium from natural materials by thermodynamic modeling in conditions of out-of-furnace steel treatment. X-rays phase and differential thermal methods of analysis were applied to investigate the samples of natural barium and strontium containing material. A process flowsheet of steel treatment by barium-strontium modifier in induction furnace was developed on the basis of carried out research.

Introduction

Application of relatively low-price modifying raw materials, which provide a purposeful control over physical and chemical state of metal melt and metal products, respectively, is one of the basic development conditions of metal production technologies. Barium and strontium containing carbonate ores mined in the North-East of Irkutsk region in Russia are considered such promising materials. Their application for modifying steel treatment makes it possible to manufacture metal products with improved operational characteristics, what is quite an urgent problem. Complex carbonate ores, containing barium and strontium are represented by barium and strontium modifier.

X-rays analysis conducted at T = 293 K has demonstrated that basic compounds, barium and strontium modifier consists of, are barytocalcite $BaCa(CO_3)_2$, calcite $CaCO_3$, calciostrontianite $CaSr(CO_3)_2$, dolomite $MgCO_3$ and siderite $FeCO_3$.

Differential thermal analysis of barium and strontium modifier has exposed that when heating moisture is removed; phase transformations take place in admixtures; dolomite, calcite, barytocalcite and calciostrontianite are dissociated. Therefore, behavior of barium and strontium oxide compounds and its analysis are the most interesting issues in terms of processes of steel treatment. Aluminum, silicon and carbon can be used as reducers at different points of steel modifying.

Software package «Terra» [2] was used for thermodynamic modeling, so equilibrium composition of multi-component, heterogeneous thermodynamic system for high temperature conditions could be determined on the basis of maximum principle of entropy.

Resolved model problems could help to determine the conditions of barium and strontium reduction from multi-component oxide systems, containing the set of elements Ba–Sr–C–O–Si–Al, represented by substances SrO–BaO–C–Si–Al. The original composition of the system was varied by setting the amount of reducers Al, Si and C from 0 to 1 kilogram. Temperature range 1873 – 2073 K was used to determine the effect of temperature.

All substances, which can form through numerical modeling at designated element composition of mixture and temperatures 1873 – 2073 K were divided into significant and insignificant ones according to their concentration in final state, significance threshold was accepted 10^{-4} mole per kg of mixture. Condensed phase containing atoms and molecules: Ba, C, Al, Si, Sr, BaO, SrO, SiO_2, $BaSiO_3$, $SrSiO_3$, $BaAl_2O_4$, $SrAl_2O_4$ belongs to significant substances.

Reduction by carbon

The results of equilibrium compositions calculation in systems Ba–O–C и Sr–O–C at temperature 1873 – 2073 K within the range C = 0 ÷ 1 kg are shown in Figures 1 and 2. Taking into consideration aforementioned calculations we can conclude that notable carbon reduction of barium from oxides begins at temperatures above 2000 K, that implements in special electro-thermal processes.
As opposed to barium strontium isn't practically reduced by carbon in considered temperature range and at designated carbon consumption.

Reduction by silicon

If silicon is used as a reducer for barium reduction, the process of reduction progresses proportionally to the amount of reducer up to 0.06 kg (Fig. 3). Approximately 60 % barium is reduced. Further increasing of the amount of reducer doesn't change reduction value of barium. When BaO and Si interact chemically both barium and $BaSiO_3$ are generated, moreover, concentration of the latter like that of barium increases simultaneously to silicon concentration growth up to 0.06 kg without any further changes. That is, if barium is reduced by silicon from oxide, approximately 30 % of oxide transforms into barium silicate ($BaSiO_3$). Temperature doesn't have a significant effect on the kinetics of barium reduction by silicon, especially at stoichiometric relationship.
Other regularities were registered when strontium was reduced from its oxide by silicon (Figure 4). The amount of reduced strontium rises slowly as silicon concentration increases in the whole designated range of reducer consumption; moreover, strontium is reduced less than barium. Even if the ratio of strontium oxide to silicon equals to 1:1, the amount of reduced strontium doesn't exceed 15 %. Strontium is reduced and at the same time strontium oxide interacts with forming silica, as the result strontium silicate $SrSiO_3$ is generated. Temperature has a slight effect on the kinetics of strontium reduction by silicon.

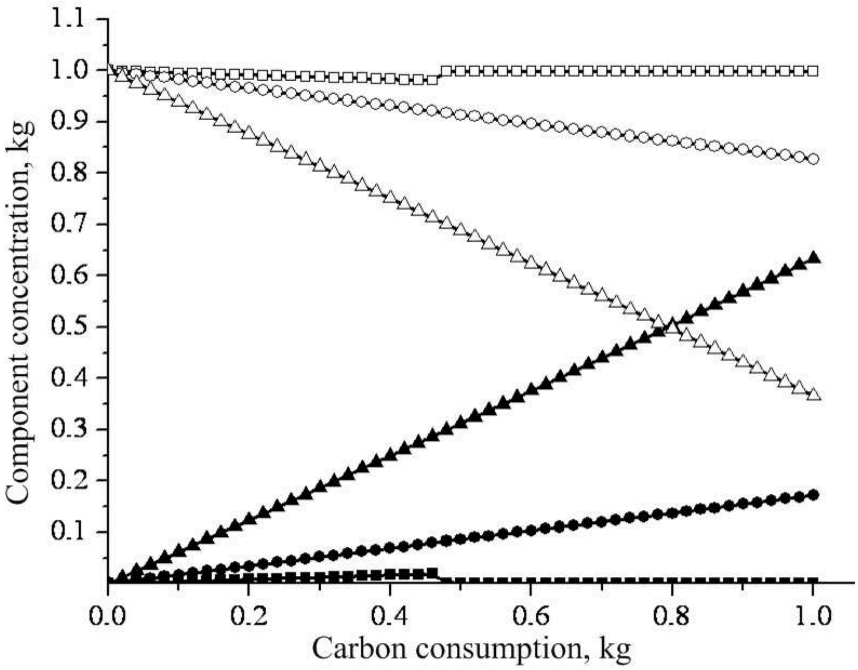

Fig. 1. Dependence of barium reduction in the system Ba - O - C on carbon consumption at temperatures 1873, 1973 and 2073 K:
—■— Ba – 1873 K; —●— Ba – 1973 K; —▲— Ba – 2073 K;
—□— BaO – 1873 K; —○— BaO – 1973 K; —Δ— BaO – 2073 K.

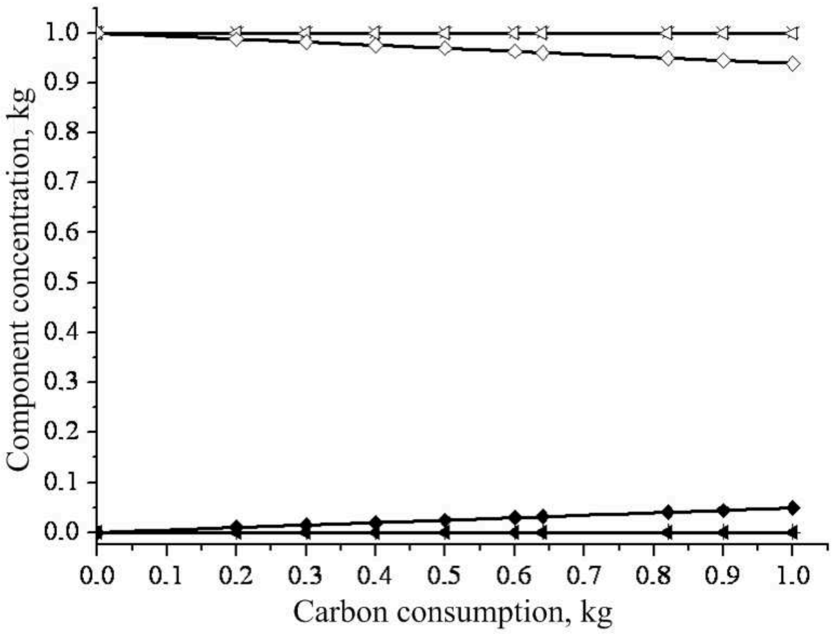

Fig. 2. Dependence of strontium reduction in the system Sr - O - C on carbon consumption at temperatures 1873, 1973 and 2073 K:
Sr – 1873 K; Sr – 1973 K; Sr – 2073 K;
SrO – 1873 K; SrO – 1973 K; SrO – 2073 K.

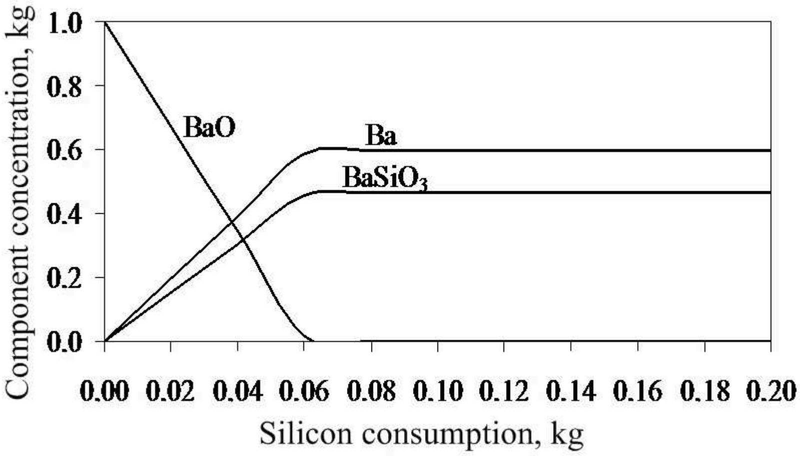

Fig. 3. Dependence of barium reduction in the system Ba - O - Si on silicon consumption at temperatures 1873 – 2073 K.

Reduction by aluminum

Barium and strontium are better reduced by aluminum than by silicon (Fig. 5, Fig. 6). The amount of barium rises linearly and the amount of BaO linearly falls up to zero if from 0 to 0.08 kg aluminum is added. The degree of barium reduction amounts to 70%. Barium and $BaA1_2O_4$ (до 0.42 kg) amounts increase simultaneously. Similar regularity is registered when strontium reducing. However, its reduction degree is 40–50 % only.
Temperature has a slight effect on the kinetics of strontium reduction by aluminum.

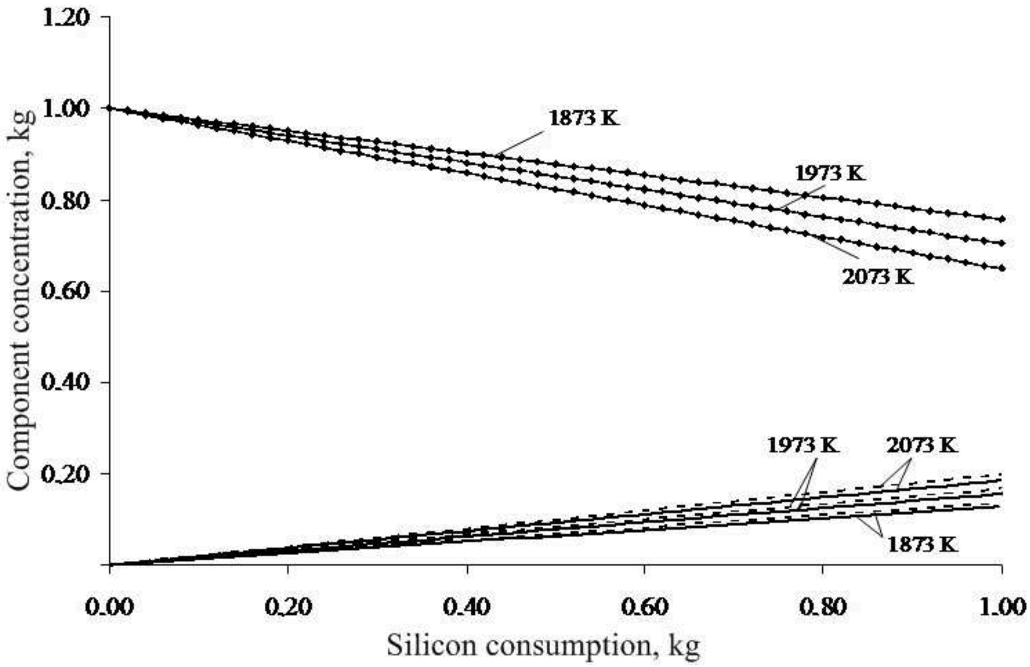

Fig. 4. Dependence of strontium reduction in the system SrO - Si on silicon consumption at temperatures 1873, 1973 and 2073 K:
—◆— SrO; ---- Sr; – $SrSiO_3$.

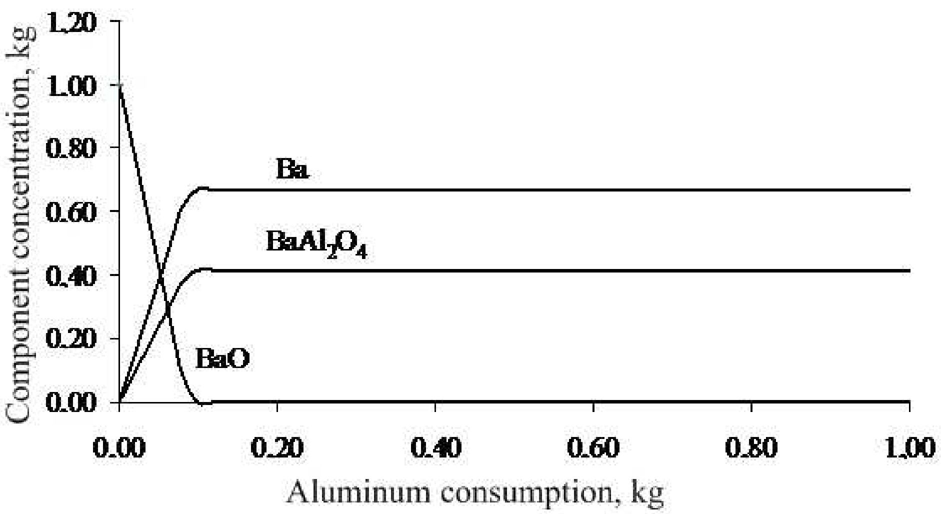

Fig. 5. Dependence of barium reduction in the system BaO-A1 on aluminum consumption at temperatures 1873 – 2073 K.

Reduction by silicon and aluminum

To assess the possibility of combined reduction by silicon and aluminum the case for reduction of 1 kg BaO and 0.2 kg Si followed by aluminum addition was calculated. Combined reduction of strontium oxide by silicon and aluminum was not considered because silicon doesn't practically reduce strontium. The data of calculation are shown in Figure 7. Aluminum addition causes decomposition of barium silicates and generation of $BaAl_2O_4$, as well increase in reduced barium concentration in the system Ba-O-Si-Al. That is, if silicon and aluminum are used together, aluminum is the main reducer.

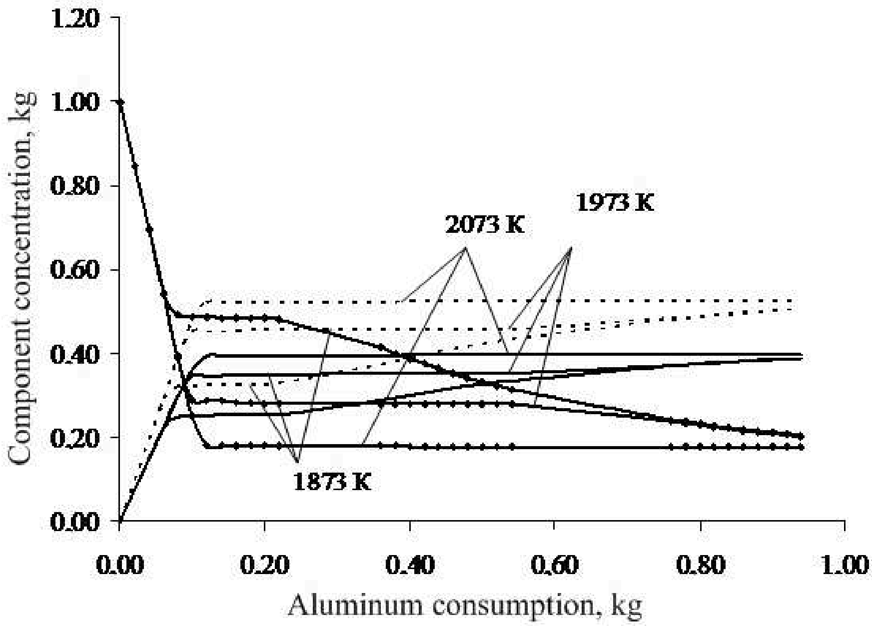

Fig. 6. Dependence of strontium reduction in the system SrO-Al on aluminum consumption at temperatures 1873, 1973 and 2073 K:
SrO; Sr; $SrAl_2O_4$.

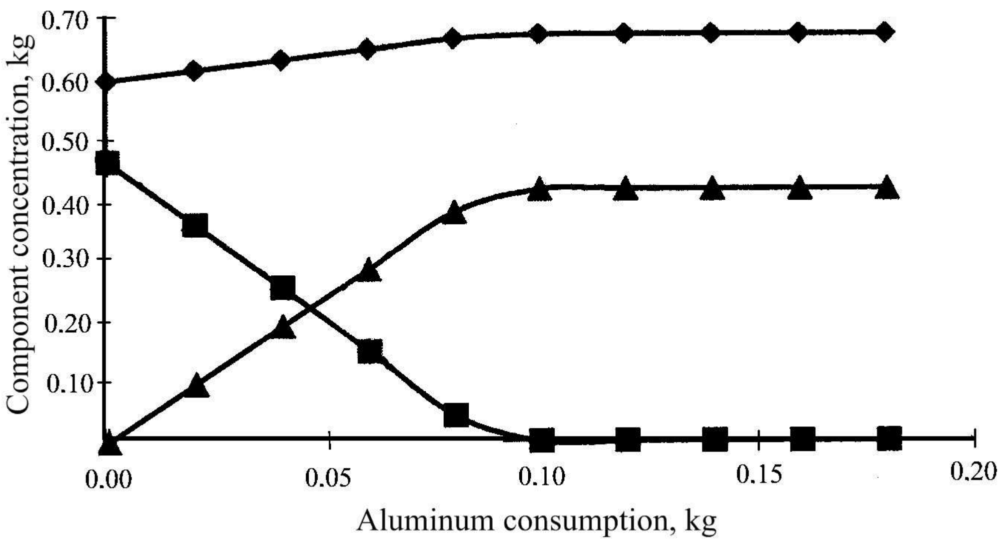

Fig. 7. Dependence of barium reduction in the system Ba - O - Si - A1 on aluminum consumption at temperature 1873 K:

Ba; $BaSiO_3$; $BaAl_2O_4$.

The technology of steel modifying by barium and strontium modifier was developed on the basis of thermal-dynamical modeling results and carried out experiments. Industrial research into the technology of 35HGSL grade steel modifying by barium and strontium modifier was carried out in induction furnace.

To modify 35 HGSL -grade steel in induction furnace pellets were applied with different chemical composition listed in the Table 1. The use of pellets containing sintered aluminum and ferrosilicon accelerates the process, waste is decreased, and utilization factor of aluminum rises up to 95 %, and that of silicon up to 85 – 90 %.

Table 1. Pellet composition

Material	Concentration [%]			
	Variant 1	Variant 2	Variant 3	Variant 4
Powder of barium and strontium modifier	57	55	54	53
Dust of ferrosilicon FS75	24	29	30,5	32
Aluminum powder	14	12	10	8
Fluorspar	2	2	2,5	3
Alkali silicate (binding agent)	3	2	3	4

The process of steel treatment by pellets is shown in Figure 8.

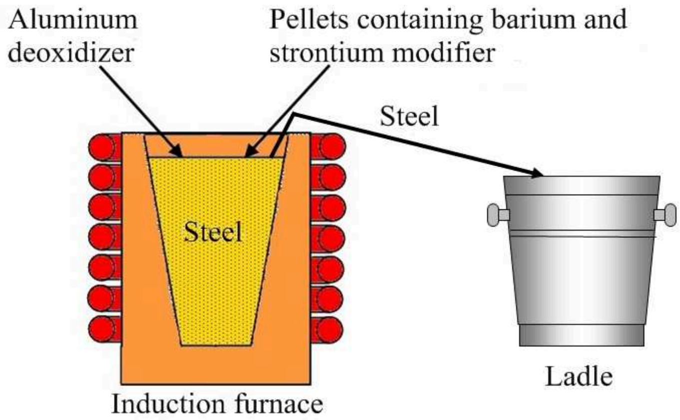

Fig. 8. Process flowsheet of steel treatment by pellets in induction furnace

Foundry goods and steel samples of test melting were heat treated according to the mode – hardening at temperature 1143 – 1153 K – tempering at temperature 863 – 923 K.
The results of mechanical tests of obtained steel samples are shown in Figure 9.

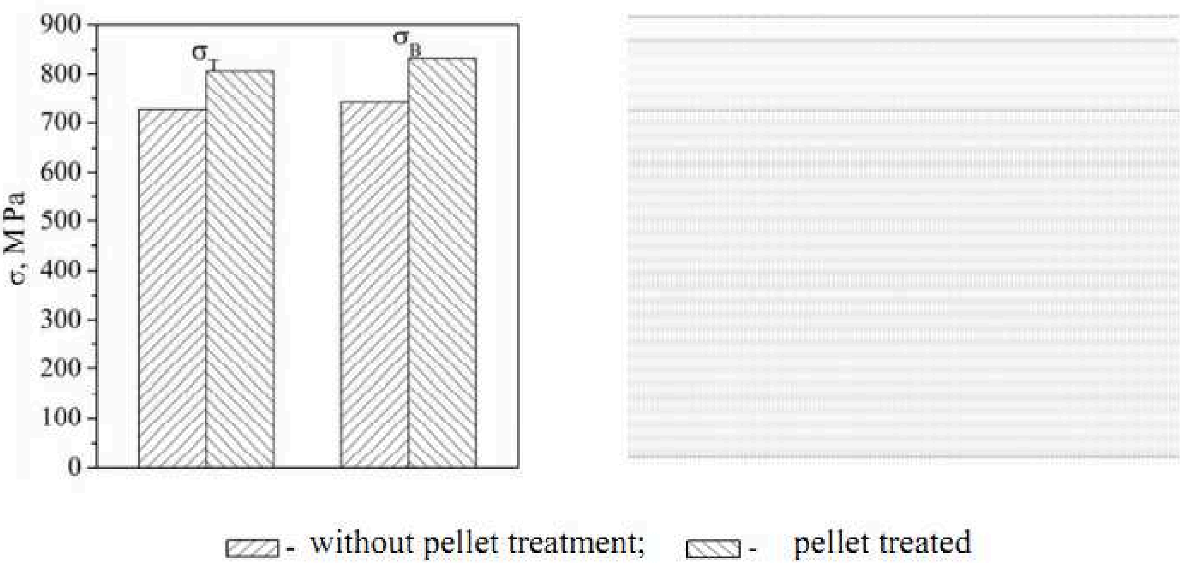

Fig. 9. Mechanical characteristics and impact strength of 35 HGSL -grade steel after hardening (1143 – 1153 K) and tempering (863 – 923 K)

Summary

Therefore, we can conclude that aluminum is to be used as a reducer in steel treatment by barium and strontium containing materials. It is naturally that for purposeful application of aluminum preliminary rigorous deoxidation of metal and slag is needed to reduce the total oxidation degree of the system metal-slag.
The results of carried out mechanical tests showed 15 – 20 % increase in service characteristics of steel, such as yield point, strength and impact strength after treatment by barium and strontium modifier in induction furnace.

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