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RESEARCH OF PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE NEW COMPLEX CALCIUM-CONTAINING FERROALLOY

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ABSTRACT

Complex ferroalloys which include alkaline earth metals (such as calcium, magnesium, barium and other metals) have particular importance for high-quality metallurgy. In addition, development of the theory and practice of modification of cast iron, cast and deformed steel stipulated necessity in creation of the new type of product — modifiers with participation of rare earth and alkaline earth elements.

Alkaline earth metals (AEM), having a high chemical affinity to oxygen and most other harmful impurities, as well as low solubility in liquid iron, are one of the most effective deoxidizers, desulfurizers, dephosphorizers and steel modifiers. The widespread use of AEM in the industry opens up real possibilities for quality improvment of steel and cast iron, reduction of the mass of metal products, rise of their operation reliability and durability and, as a result, significant metal savings.

Previously the authors have developed the experimental batch of complex ferroalloy containing calcium, barium and magnesium with the following chemical composition, %: Ca — 11–15, Si — 50–55, Al — 12–20, P — 0,06, S — 0,02, Mg — 1,2, Ba — 1,3 and Fe is the rest. This ferroalloy was obtained as a result of large-scale laboratory tests simulating industrial conditions at the experimental site of Chemical and Metallurgical Institute named after Zh. Abishev.

Efficiency of application of each new ferroalloy for deoxidation, microalloying and steel modification is determined primarily by its various characteristics (chemical and phase composition, mineralogy, thermal properties, etc.). Correspondingly, the current research is based on different studies that were carried out for the obtained calcium-containing ferroalloy, including the following ones: investigation of the phase composition by X-ray phase analysis, study of phase transformations during heating by the differential thermal analysis, determination of mineralogical composition and density by metallographic studies and by the pycnometer method.

Introduction

Efficiency and expedience of use of any ferroalloys is determined not only by their chemical composition (concentration of the basic elements and accompanying impurities), but also by physical and chemical properties (granulometric composition, density, surface quality, melting temperature, content of non-metallic inclusions, oxygen, hydrogen etc.) [1].

Practice of steelmaking works testifies about necessity of accounting not only chemical composition of ferroalloys during their quality evaluation, but also their physical properties (melting temperature, density etc.) that mainly determine efficiency of alloying in a steel bath. The following main requirements can be emphasized from the point of view of efficiency of ferroalloys use at operating production sites [1–5]:

1. Ferroalloy composition should be in correspondence with economical efficiency and technological features of its fabrication and use.

2. Optimal density of ferroalloys. At present time more than 95% of all ferroalloys is introduced in liquid steel as lumps. Ferroalloys having optimal density are mostly completely involved in hydrodynamic motion by steel flows in a ladle and. as a result they are subjected to most quick and complete melting with complete recovery in steel. Large difference between densities of ferroalloy and alloying metal is unacceptable. Optimal density of ferroalloys is located within the range 6–8 g/cm^3 (according to the data of the authors [5]).

3. Ferroalloys should have mechanical properties providing satisfactory crushability in forming the minimum of fine fractions; ferroalloys should also be characterized by low porosity, flowability and segregation values of the elements in an ingot, which have to meet the customer's requirements in granulometric composition and visual sight.

Complex ferroalloys containing alkaline earth metals (AEM) — calcium, magnesium, barium and other metals have especial importance for the quality metallurgy. Additionally, development of theory and practice of modification of iron, cast and deformed steel initiates necessity of creation of the new products — modifiers with participation of rare earth and alkaline earth elements [6, 7].

Several authors proved efficiency of use of ferroalloys with AEM for steel deoxidation and modifying [8–14]. E.g., the researches [8, 9] described qualitative parameters of the alloys containing calcium, magnesium, barium and other alkaline earth elements and rare earth elements in ferroalloys. These authors established that such elements provide not only high-efficient steel deoxidation, but also removal of non-metallic inclusions s well as improvement of mechanical properties of finished products.

Taking into account the above-mentioned declarations, it is evident that the complex of comprehensive investigations of physical and chemical properties and features of the new ferroalloy grades is strictly needed. Thereby, the aim of this research is conduction of the detailed examination of the physical properties of the new complex ferroalloy.

Methods and materials

Previously we have conducted invstigations[1, 2] on examination and mastering the technological process of melting of complex ferroalloy with alkali earth metals (calcium, barium and magnesium) from dump blast furnace slag, using high-ash coal (with ash content more than 45%) from Saryadyr deposit and coal slime from Karaganda basin [15].

Melting experiments were conducted at the experimental site of Chemical and metallurgical institute named after Zh. Abishev, in the single-phase electric arc furnace with current-conducting bottom that simulates the industrial conditions. The ore smelting furnace is equipped with two transformers switched in parallel, with total nominal capacity 0.2 MVA. The arc discharge temperature was within the range 2500–5000 °C and was provided by graphite electrode with 150 mm diameter.

The following materials were used as initial raw materials for production of complex calcium-containing ferroalloy:

– dump blast furnace slag (size of fractions 10–40 mm) received from ArcelorMittal Temirtau (Temirtau, Kazakhstan), with average chemical composition as follows, %: SiO_2 3.55, Al_2O_3 14.61, CaO 34.12, MgO 11.2;

– high-ash coals with the following chemical composition, %: solid carbon 40–45, ash content more than 45, volatile compounds 10–14; chemical composition of coal ash makes, %: SiO_2 60–64, Al_2O_3 30–35; specific heat of coal burning is 7,500–8,000 thousand kcal/kg, specific consumption of high-ash coal per 1 ton of calcium-containing ferroalloy was 2.72 t.

Additional charging by other materials was not done. Alloy tapping was conducted in iron moulds, average weight of an alloy bulk was 11 kg; it was noted that the alloy didn't fall into pieces. Comminution in a jaw crusher was conducted for alloy blending, where forming of fines (fractions with the size less than 10 mm) made not more than 10% from total mass.

As a result, the pilot party of calcium-containing ferroalloy with other elements, including AEM was prepared. Its chemical composition was within the following range,%: Ca 11–15, Si 50–55, Al 12–20, P 0.06, S 0.02, Mg 1.2, Ba 1.3 and Fe for the rest.

The current research includes several conducted investigations of the obtained alloy, i.e. study of its phase composition, phase transformations during heating, mineralogical composition and density.

X-ray phase analysis was used for identification of phase composition in the alloy samples. X-ray diffraction shooting was conducted at DRON-2 diffractometer, in the conditions of Cu radiation filtering, with tube voltage 30 kWt and tube current 30 mA. The obtained X-ray photographs of the samples were identified in accordance with the ASTM catalogue in manual mode. Reliability of the catalogue and its operating technique for the specialists are confirmed by the reference samples.

The method of differential and thermal analysis (DTA) was used for examination of chemical reactions and physical transformations, occurring under heat pressure in the alloy between its single compounds. DTA was conducted in the air oxidizing atmosphere, using derivatograph of F. Paulik, I. Paulik, L. Erdei system, that allows to measure mass variation (TG) and rate of mass variation (DTG) for the sample, as well as temperature difference between the examined and inert samples in the conditions of continuous heating with preset rate. The heating rate made 10 grad per min.

Density of the examined ferroalloys was determined via the picnometric method based on variation of liquid massv with metal powder.

Metallographic examination of the structure of ferroalloys obtained via carbothermal method from dump metallurgical slag was conducted using scanning electronic microscope of JEOL-JSM7001F type. This microscope is the unique device because it automatically determines the chemical composition from the spectrum and makes it possible to determine the phase using chemical composition of the preset point.

Obtained results and their analysis

The results of conducted X-ray phase analysis of ferroalloy pilot samples are presented by the X-ray photographs (**Fig. 1**).

It was established based on the data obtained via X-ray phase analysis that phase composition of the pilot samples is presented mainly by $CaAl_2Si_{1.5}$ and free silicon.

Differential and thermal analysis of the samples of obtained ferroalloy was conducted during the researches.

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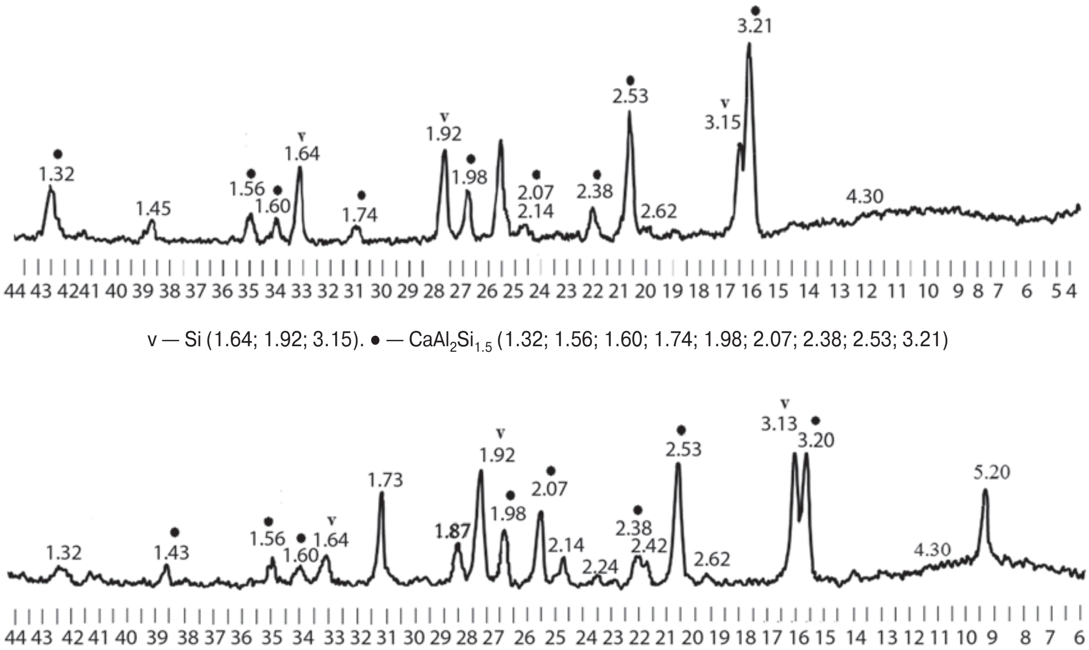
[1] Experiments on melting of complex ferroalloys with rare earth metals via carbothermal method in semi-industrial conditions: intermediate report on R&D work. Affiliate of Republic State Enterprise (RGP) on the right of economic jurisdiction (PKhV) "National Center for Complex Processing of Mineral Raw Materials of Kazakhstan Republic" "Chemical and metallurgical institute named after Zh. Abishev": director Baisanov A. S..; executor.: Makhambetov E. N., Karaganda. 2019. 49 p. No. GR 0118PK0069. Inv. No. 0219PK00253.

[2] Choice of optimal compositions of charge materials and melting conditions for complex ferroalloys with alkali earth metals: intermediate report on R&D work. Affiliate of Republic State Enterprise (RGP) on the right of economic jurisdiction (PKhV) "National Center for Complex Processing of Mineral Raw Materials of Kazakhstan Republic" "Chemical and metallurgical institute named after Zh. Abishev": director Baisanov A. S..; executor.: Makhambetov E. N., Karaganda. 2018. 50 p. No. GR 0118PK0069. Inv. No. 0218PK00757.



v — Si (1.64; 1.92; 3.15). ● — $CaAl_2Si_{1.5}$ (1.32; 1.56; 1.60; 1.74; 1.98; 2.07; 2.38; 2.53; 3.21)

v — Si (1.64; 1.92; 3.13). ● — $CaAl_2Si_{1.5}$ (1.43; 1.56; 1.60; 1.74; 1.98; 2.07; 2.38; 2.53; 3.20)

Fig. 1. Examples of X-ray photographs for the calcium-containing ferroalloy

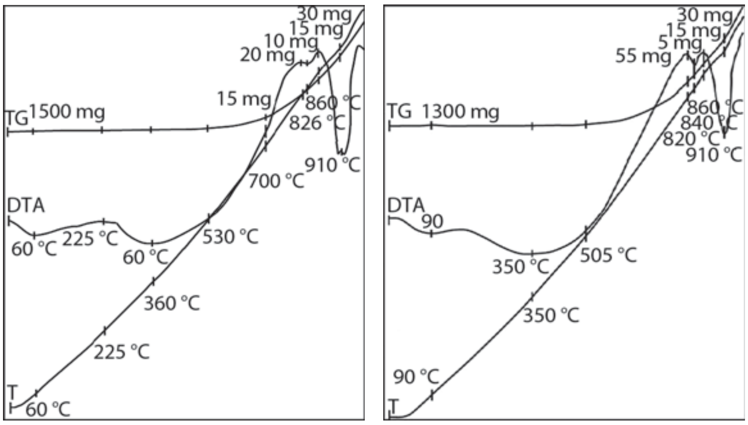


Fig. 2. Examples of derivatograms of the alloy pilot samples

Table 1. **Composition of spectra of the examined ferroalloy**

Sample number	Spectra	Content of the elements in atomic weights,%					
		Al	Si	Ca	Mn	Fe	Ba
1	Spectrum 1	22	63.6	10.5	–	3.5	–
2	Spectrum 1	22	62.9	12.6	–	2.8	–
3	Spectrum 1	12	72.9	6.6	–	5.5	–
4	Spectrum 1	19.4	64.9	3.3	0.1	0.1	12.2
	Spectrum 2	1.1	62.1	0.0	32.1	4.8	0.1
	Spectrum 3	0.9	66.3	32.5	0.1	0.0	0.1
	Spectrum 4	39.2	40.2	20.3	0.1	0.1	0.1
	Spectrum 5	0.1	99.8	0.0	0.0	0.0	0.0

The derivatograms of the pilot ferroalloy are presented on the **Fig. 2**.

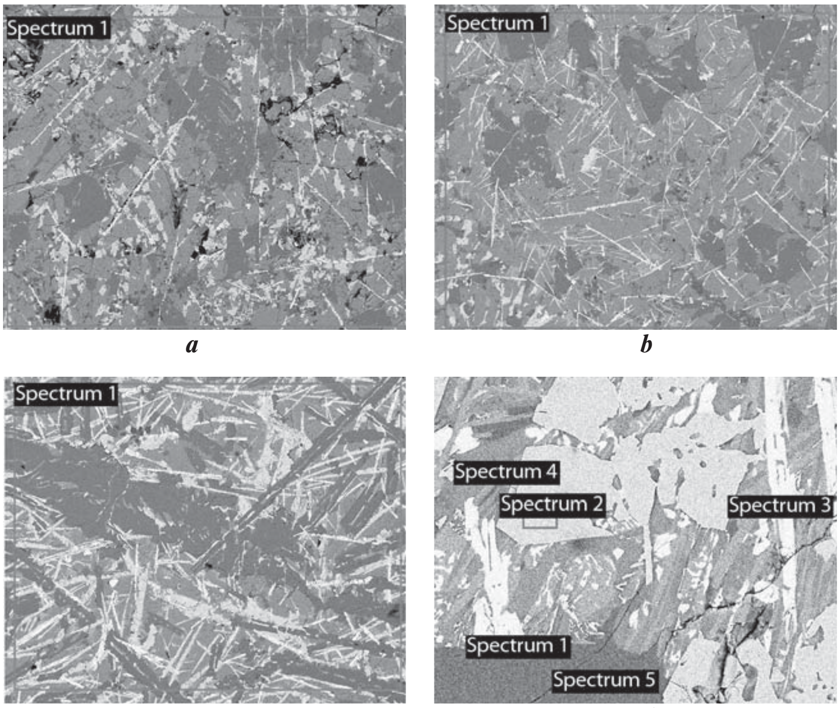
Two endothermic effects were revealed on derivatograms of the alloy pilot samples within the temperature range 60–530 °C. Increase of sample mass occurs starting from the temperature 530 °C; it can be connected with the primary oxidation of the elements which takes place with exothermic effect within the temperature range 530–860 °C. The distinctly expressed endothermic effect was revealed at the temperature 910 °C; it can be caused by destruction of alloy crystalline structure melting that occurs with heat absorption.

The ferroalloy density occupies the especial place among the most important physical and chemical characteristics of the alloys. It has significant effect not only on the process of ferroalloy production, but also on degree and stability of fixation of the leading elements, on their dissolution rate and homogeneity of distribution in metal volume. It was revealed as a result of tests for density determination via picnometric method that the obtained ferroalloy density makes 3.5–4.5 g/cm^3.

Metallographic study of the structure of four ferroalloy samples helped to reveal composition of spectra of the examined pilot complex alloy (**Table 1**).

Distribution of the elements in the phases of complex ferroalloy is illustrated by the scanning data (**Fig. 3**). Metallographic analysis shows that the ferroalloy is presented by three structural components that are emphasized by different colours: white (narrow and long needles of dendrite structure), gray (the main square with round form), dark gray (matrix).

It is clear from the Fig. 3, *d* that spectrum 1 of the sample No. 4 is presented by the phase of bright white colour, occupies small square and is characterized by barium



a *b* *c* *d*

Fig. 3. Structure of the examined ferroalloy with different magnification:
a — sample No. 1; *b* — sample No. 2; *c* — sample No. 3; *d* — sample No. 4

presence (see Table 1). This spectrum corresponds in its chemical composition to $Ba(SiAl)_4$ phase. Spectrum 2 is presented by light gray colour, occupies about 20% of square and corresponds by his visual features and chemical data to the phase (SiMn), or manganese silicide. However, according to X-ray phase analysis (see Fig. 1), manganese and barium are not revealed in this alloy both in structurally free form and in the form of intermetallic compound.

Spectrum 3 displays eutectics with light gray matrix; it corresponds to calcium disilicide phase ($CaSi_2$) according to the data of electronic parameters and chemical analysis. Spectrum 4 occupies about 40–50% of square, and microstructure of this phase is characterized by fine differentiated eutectics, in addition to free silicon and iron disilicide. This eutectics was defined as ($CaAl_2Si_{1.5}$) phase based on the results of complex X-ray structural, microstructural and electronic analysis. Spectrum 5 is presented by dark gray colour, and presence of free silicon (up to 99.8%), identifying as structurally free silicon, is the feature of this phase.

Conclusions

It was established on the base of the results of conducted researches that active elements элементы (Mn, Si, Al и Ca) are presented in the experimentally obtained complex ferroalloy in the form of complicated intermetallic compounds (such as $CaAl_2Si_{1.5}$). It excludes forming of corundum agglomeration, having negative effect on metal mechanical properties, and supports spheroidization of oxide inclusions during deoxidation and modification of both ordinary and quality steels. The temperature of alloy melting (crystallization) was revealed on the base of differential thermal analysis (910 °C). Density of the examined alloy was also determined, it is within the range 3.5–4.5 g/cm³.

The obtained data on investigation of physical and chemical properties of the new complex calcium-containing ferroalloy make it possible to suggest the conclusion about possible economical and technological expedience of fabrication of complex ferroalloys containing calcium, barium and magnesium from dump blast furnace slag, using high-ash coal delivered from Karaganda basin.

Conduction of consequent researches of this alloy and putting it into practice in the real industrial conditions as steel deoxidizer and modifier is strictly required for establishment of economical and technological efficiency of the obtained calcium-containing ferroalloy.

Presented results were obtained during execution of the scientific and technical program No. BR05236708 "Scientific and technological substantiation of widening of raw material base of the ferroalloy industry owing to involvement of slightly coking power generating coals and man-caused wastes in order to receive the new materials of multi-purpose destination", within the framework of the contract for the programmed and aimed investment for 2018–2020 with the Scientific Committee of the Ministry of Education and Science of Kazakhstan Republic and grant investment of the scientific researches for 2018–2020 with the Scientific Committee of the Ministry of Education and Science of Kazakhstan Republic on the theme AP05130225.

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