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ИЗУЧЕНИЕ ЖЕЛЕЗНЫХ РУД АЯТСКОГО МЕСТОРОЖДЕНИЯ ООЛИТОВОГО ТИПА

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Аннотация: представлены результаты исследований состава оолитовой железной руды Аятского месторождения. Проведены эксперименты и представлены результаты исследования разложения бурого железняка в окислительной атмосфере. Анализ химического состава исходной и обожженной руды проводили с помощью электронного микроскопа (микрорентгеноспектральный анализ), а также химическим методом. Изучение минералогического состава исходной и обожженной руды проводили на дифрактометре методом рентгеноструктурного анализа. Полученные данные необходимы для разработки теоретических и технологических основ пирометаллургической переработки оолитовых железных руд с высоким содержанием фосфора.

Ключевые слова: оолитовая железная руда, фосфор, Аятское месторождение, окислительный обжиг, распределение элементов в руде, железосодержащая фаза.

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Study of the iron ores of the Ayat deposit of the oolite type

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Abstract: The paper presents the results of studies of the composition of the oolitic iron ore of the Ayat deposit. Experiments were carried out and the results of the study of the decomposition of brown ironstone in the oxidizing atmosphere are presented. Analysis of the chemical composition of the initial and burnt ore was carried out using an electron microscope (micro X-ray spectral analysis), and also by the chemical method. The study of the mineralogical composition of the initial and burnt ore was carried out on a diffractometer by X-ray diffraction analysis. The obtained data are necessary for the development of theoretical and technological bases of pyrometallurgical processing of oolitic iron ores with high phosphorus content.

Key words: oolitic iron ore, phosphorus, Ayat deposit, oxidative firing, distribution of elements in ore, iron-containing phase.

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1 Introduction

The main trends in the development of the modern mining and metallurgical complex are determined by the need for extensive involvement in the processing of technogenic waste [1—2], complex and hard-to-enrich ores [3—7]. The latter include oolitic iron ores with an increasingly complex mineralogical composition or with an increased phosphorus content [8—10]. According to statistics, at the current production rates, high-quality iron ores with a phosphorus content below 0.05 wt. % will be depleted within 30 years [11—12]. Thus, there is a need to use iron ore raw materials with a high phosphorus content. At the same time, such ores are located all over the world in fairly large deposits. One of the largest deposits of oolitic iron ore in Russia and the world is the Bakcharsk deposit in the Tomsk region, with reserves of 28.7 billion tons [13]. Loose and dense goethite-hydrogetite types of iron ores, which contain 38—42% iron, 1.03—1.3% phosphorus, and 0.13—0.25% vanadium, are most common in the Bakcharsk deposit [14]. Russia also has the Kerch iron ore basin (18 billion tons), which is formed by iron ores with an oolitic structure. This ore contains 37.5% iron, 0.9—1.3% phosphorus, up to 0.6% V, about 0.5% sulfur, and 0.5% arsenic [15].

In Kazakhstan, there are Lisakovsk (1.6 billion tons) and Ayat deposits (more than 10 billion tons) of brown iron ores [16—17]. The brown ironstone ore of the Lisakovsk deposit in the Kostanay region contain up to 35.4% iron, 0.7% phosphorus, 0.08% sulfur, and 0.06—0.08% vanadium [18]. The Ayat iron ore basin is also located in the Kostanay region. The deposit was discovered in 1899 but is still not exploited. The ore of this deposit contains fine-grained oolites of various types. The main minerals of the Ayat ores are goethite (20—60%), leptochlorite (11—44%), siderite (3—50%). The main non-metallic minerals are glauconite and clay minerals, secondary — pyrite, marcasite, manganese hydroxides, magnetite, quartz, feldspar, tourmaline, zircon, apatite, chalcedony. The iron content is 32—40%, and its concentration in oolites is higher than in ore cement. The amount of silica and alumina, respectively, ranges from 12—22 and 3—10%. Of the impurity elements, sulfur (up to 0.36%), phosphorus (from 0.3% to 0.5%), vanadium (up to 0.14%), manganese (less than 1.0%) and magnesium (from 0.3% to 1.2%) should be noted. Ore cement is richer in sulfur, magnesium, and manganese: it contains sulfides, clay minerals, and siderite. Phosphorus is characteristic of oolites, where it correlates with the oxide form of iron [19].

In terms of iron content, the oolitic iron ores of the Ayat deposit are close to the brown iron ores of the Kerch, Bakcharsk, and Lisakovsk deposits, but their phosphorus content is lower. It is also worth noting that Ayat ores are richer than Lisakovsk ores in terms of vanadium and aluminum content. Compared with some foreign ores, their iron content is higher, and there is no lead in them.

In our previous works [20—22], thermodynamic calculations and preliminary experiments on solid-phase selective reduction of phosphorus and iron were carried out, in which metallic iron with low phosphorus content can be obtained. For further research and development of theoretical and technological foundations of pyrometallurgical processing of oolitic iron ores with high phosphorus content, a comprehensive study the features of the initial sample is necessary.

The purpose of this work is to study the morphology of the oolite ore of the Ayat deposit and the processes of transformation of its structural components during oxidative burning.

2. Research object and methodology

Due to the fact that the Ayat deposit is still undeveloped, the ore sampled from the top weathered layer of the deposit was used as an object of study . The ore has a heterogeneous loose and lumpy structure (Fig. 1). The lumpy part consists of oolites bound by clay-cement mass. The loose ore part consists of fragments of oolites and micrograins of quartz and alumina.

Ore grains are small rounded concentric-shell formations, so-called oolites, whose sizes are mainly in the range from 0.25 to 0.80 mm, and individual oolites reach to 1 mm. The structure of the otoliths in the ore is explained by their sedimentary origin. It is assumed that it was formed at the stage of sedimentogenesis in the coastal-marine environment under conditions of significant hydrodynamic activity with the participation of the biogenic factor.

The study of the initial material included the study of the chemical and mineral composition of particles, the transformation of ore during heating, the construction of maps of the distribution of elements in ore particles. Chemical, micro-X-ray spectral and X-ray phase analysis by «wet» chemistry methods, scanning electron microscopy complex Jeol JSM-7001F, EDS Oxford INCA X-max 80, WDS Oxford INCA WAVE, EBSD, and HKL were used.

The initial composition of the ore was studied by chemical methods (GOST 32517.1—2013, GOST 32599.2—2013, GOST 32518.1—2013, GOST 23581.16—81, GOST 23581.9—79). To study the sequence of transformations in the ore during heating, experiments were carried out in the Nabertherm weighing muffle furnace with the possibility of continuous monitoring of the temperature and mass of the sample. At the same time, a corundum crucible was placed in the working area of the furnace, into which ore powder was poured, heated at a speed of 300°C / hour to a temperature of 1200°C, and kept for 60 minutes. For the study on optical and electron microscopes, the samples of the initial and burnt ore were filled with epoxy resin, ground, and polished. The chemical composition of the structural elements in the samples of the initial and burnt ore was determined by the microentgenospectral method on an electron microscope.

Fig. 1. Oolitic iron ore of the Ayat deposit

To determine the phase composition of the samples of the initial and burnt ore, an X-ray phase analysis was performed on an X-ray diffractometer Rigaku Ultima IV. The results were processed using «Match!» software.

3. Results and discussions

The results of the study of the chemical composition of the samples of the initial and burnt ore by wet chemistry methods are presented in Table 1.

The resulting chemical composition of the main component is close to the average composition of the oolitic iron ore of the Ayat deposit [23—24].

Fig. 2 shows the results of monitoring the mass of the ore sample during heating, and Fig. 3 shows the results of decoding the X-ray of ore samples.

The main phases of the initial ore, i.e., goethite FeO(OH) and quartz SiO_2, $AlPO_4$,

Table 1
Chemical composition of ore, mass. %

Samples	Mass fraction, %							
	CaO	MgO	Al_2O_3	Fe_{total}	SiO_2	C	S	P
Initial ore <0.4 mm	4.3	1.0	10.3	39.3	21.7	1.1	0.8	0.30
Fired ore <0.4 mm	4.2	1.6	11.8	48.1	25.2	0.2	1.0	0.31

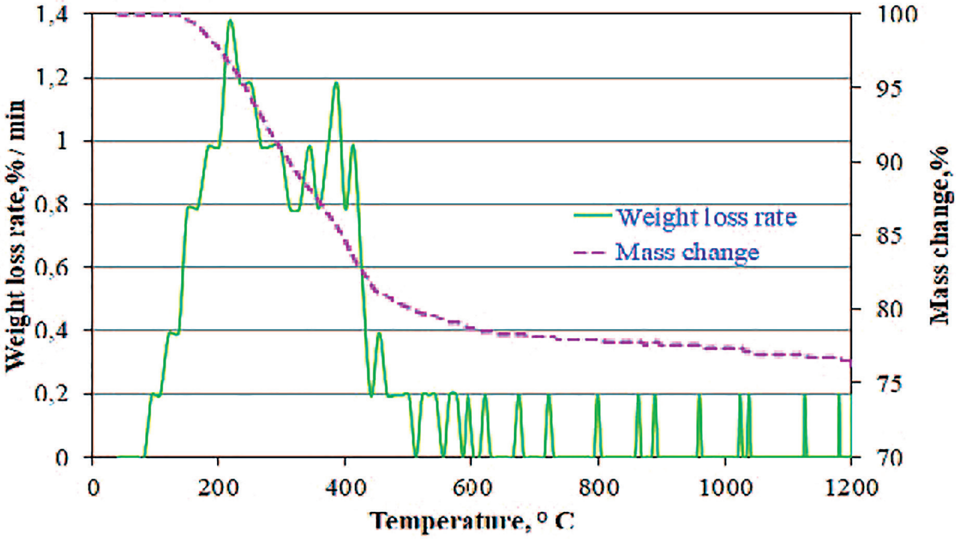

Fig. 2. Change in the mass of the starting material during oxidative burning

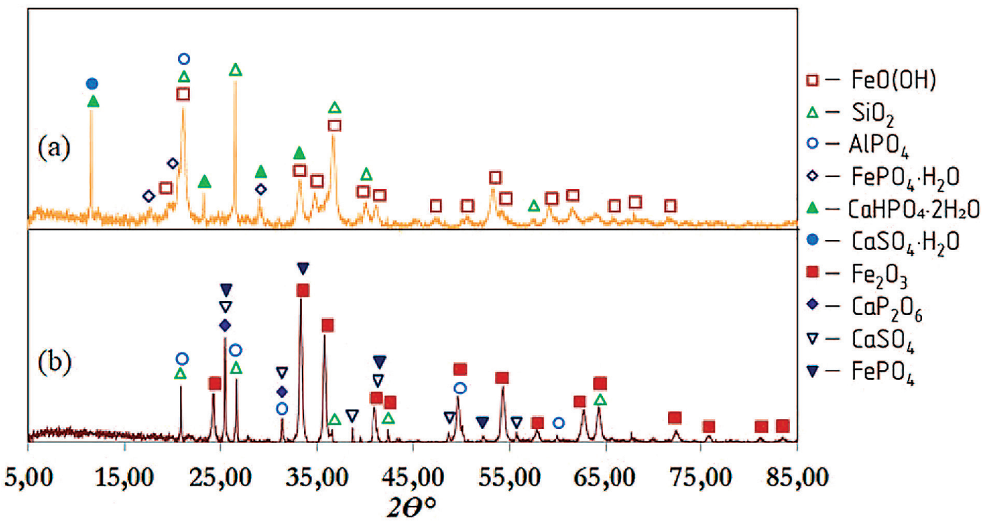

Fig. 3. X-ray of the initial (a) and burnt (b) ore

and SO_8 are well detected. The intensity of peaks of other phases of the X-ray was low, which did not allow with sufficient accuracy to determine the phases based on calcium, magnesium, and other elements with content less than 10 wt.%.

Three characteristic sections can be distinguished on the temperature dependence graph: less than 200°C, from 200°C to 600°C and more than 600°C. Taking into account the mineral composition of the initial ore, it can be assumed that dissociation of iron hydroxides and carbonates occurs on the first site, and dissociation of the remaining carbonates occurs on the second site [25]. The temperature increase above 600°C is accompanied by insignificant loss of ore mass, at prolonged exposure (1 hour) at 1200°C the mass of the concentrate does not change. The total mass change was 23.8%.

Analyzing the graph of the dependence of the rate of change in the mass of ore on the temperature, we can distinguish several peaks of the rate. At 217°C the mass-loss rate reaches a maximum and is 1.38%/min, and at 386°C, a maximum mass-loss rate of 1.18%/min is found. In the temperature range of 465 — 1200°C, the mass-loss rate is between 0.2 and 0%/min.

According to the results of X-ray phase analysis, during oxidative heating, goethite FeO(OH) loses water and turns into hematite Fe_2O_3, sulfur passes into the gas phase, and phosphorus in the firing product is present in the form of the same compound $FePO_4$, $CaPO_4$, $AlPO_4$. Taking into account the results of mass change, the rate of mass change during firing, and X-ray phase analysis, it can be assumed that the release of crystallohydrate moisture during the decomposition of goethite is completely finished when the firing reaches 250°C. In the temperature range of 300 — 450°C, the dissociation of iron carbonates occurs. At further increasing the temperature, dissociation of calcium and magnesium carbonates occurs, as well as, possibly, oxidation of sulfur and formation of sulfides. The use of optical and electron microscopes made it possible to identify the structural components of the ore and analyze the changes occurring in them during oxidative heating.

Fig. 4 shows the distribution maps in the original ore of the main elements, which are present in significant quantities. It can be seen that some of the elements (Fe, Ca, Si, Al) can be visually correlated with the structural elements presented in the photo. Thus, oolites are formed mainly by iron oxides. Other phases consist mainly of silicon and aluminum oxides. In addition, there are also complex phases, in which several elements (Fe, Si, Al) are present at once. Sulfur and phosphorus are distributed almost uniformly over the entire area of the photograph, and it is almost impossible to attribute them to any particular phase.

Fig. 5 shows photographs and points of micro-X-ray spectral analysis of structural components in the initial and burnt ore states, and the results of micro-X-ray spectral analysis of structural components are presented in Table. 2.

The iron ore of the Ayat deposit in its original form and after firing is non-magnetic.

4. Conclusion

1) The main ore mineral is goethite, the non-metallic ones are quartz and clay cement. In iron content, the Ayat ores are similar to the Kerch, Lisakovsk, and Bakchar oolite ores, but differ in lower phosphorus content.

2) Phosphorus in the ore is in the form of aluminum phosphate, as well as dissolved in iron-bearing minerals.

3) When calcined in an oxidizing atmosphere, goethite loses crystalline

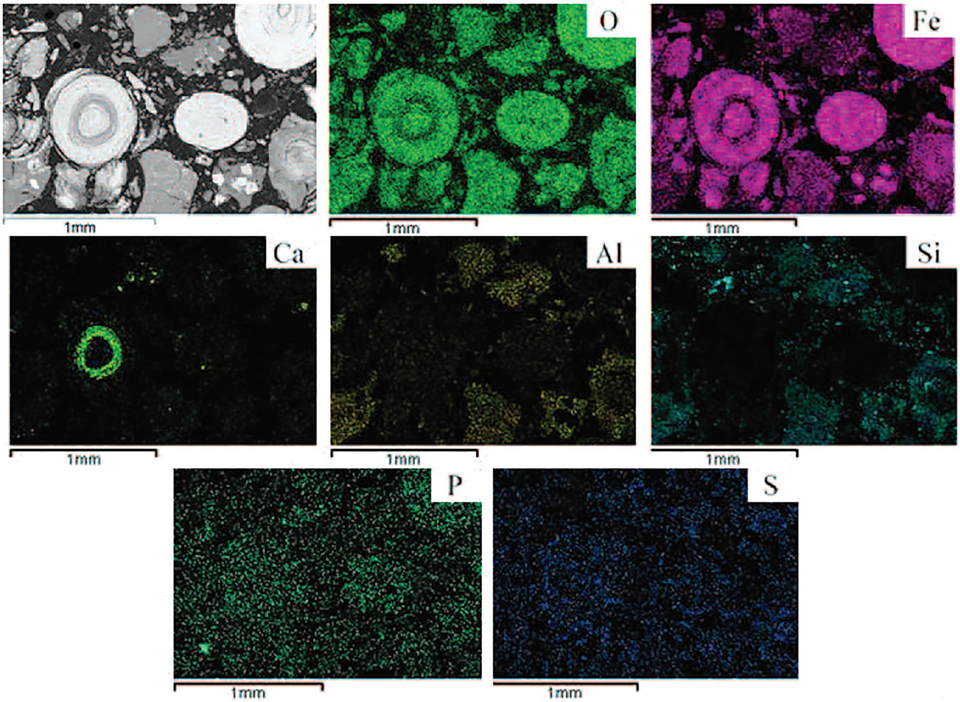

Fig. 4. Maps of the distribution of elements in the source ore

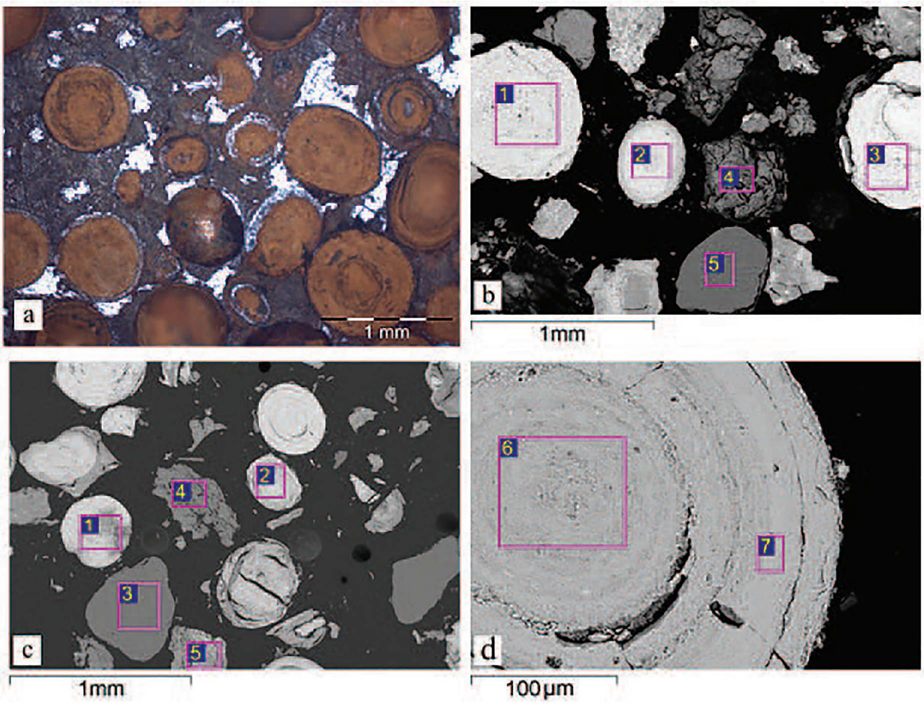

Fig. 5. Structural elements of the initial ore (a and b) and after firing (c and d.)

Table 2
Chemical composition of the initial and fired ore (at. %) at the analysis points

	O	Mg	Al	Si	P	S	Ca	Fe
1b	51.4	0.4	2.6	2.4	0.3	0.0	0.6	42.3
2b	49.0	0.3	3.7	2.0	0.4	0.0	0.1	44.6
3b	58.0	0.3	4.3	2.3	0.3	0.0	0.3	34.5
4b	59.7	0.5	9.4	20.1	0.0	0.0	0.5	10.0
5b	58.0	0.0	0.0	41.9	0.0	0.0	0.1	0.0
1c	67.1	0.1	3.8	1.7	0.5	0.0	0.1	26.7
2c	66.6	0.3	3.4	2.3	0.7	0.0	0.1	26.6
3c	71.1	0.0	0.0	28.9	0.0	0.0	0.0	0.0
4c	69.0	0.5	10.7	17.7	0.0	0.0	0.2	1.9
5c	66.0	0.7	4.6	7.8	0.7	0.1	0.3	19.9
6d	66.8	0.1	3.8	1.8	0.6	0.1	0.1	26.7
7d	67.5	0.1	3.2	1.2	0.5	0.0	0.1	27.4

chemical water and turns into hematite, carbonates dissociate. . As a result of these processes, the mass loss is approximately 24% and the concentration of iron and phosphorus in the ore increases.

4) The data obtained provide complete information about the ore and can serve as a basis for the development of pyrometallurgical processing technology of oolitic iron ore from the Ayat deposit.

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