

EXTRACTION OF IRON FROM BAKAL SIDERITE BY MEANS OF SELECTIVE REDUCTION IN A COMPLEX OXIDE CRYSTAL LATTICE

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76, Lenin ave, Chelyabinsk, Russia 454080, e-mail: salihov@nxt.ru**ABSTRACT**

A decomposition process of complex carbonate (sideroplesite) with formation of complex oxides (Fe,Mg,Mn)O and (Fe,Mg,Mn)O·Fe₂O₃ precedes the process of iron reduction from siderite ore of Bakal's deposit. The weight loss reaches 32% and a large amount of pores forms in a pieces of ore as a result of dissociation. It is believed that a large number of pores allow to reduce this ore easily, because the pores and micropores provides deep penetration of reducing carbon monoxide in the bulk of ore pieces. Throughout the experiments, it is discovered that distribution of a recovery process and separation of a metallic phase are not connected with pores. Reduction develops by an electrochemical mechanism and the channels of reduction process distribution are oxides of experimentally non-reducible metals – mainly magnesium and silicon.

High rate of iron reduction from the complex iron-manganese-magnesium oxides is explained by the high rate of distribution of negatively charged anion vacancies, forming on the surface of oxide and a reducing agent interaction.

KEYWORDS: *Sideroplesite, solid phase reduction, anion vacancies.*

1. INTRODUCTION

The existing technologies of extracting iron and other metals from ores, which are used in the form of ferroalloys in steel production, are based on theoretical backgrounds, which have been accumulating for the centuries of blast-furnace process development experience. Reduction of metals in blast and ore thermal ferroalloy furnaces takes place in the result of removing oxygen from the ore oxides by carbon. As while the temperature is rising, the oxygen affinity of carbon is increasing and the oxygen affinity of recoverable metals is decreasing, the reduction processes are carried out at possibly high temperatures in order to create the most correct thermodynamic conditions. At that, the temperature must provide not only metal reduction but also its melting, as well as melting of oxide residual. As the melting point of oxide residual is as a rule essentially higher than the melting point of metal, the other metals oxides are added in a furnace burden of reducing aggregates for the formation of multicomponent slags possessing necessary physical and chemical properties. Application of slag-forming and fluxing additions leads to the increase of expenses for their yield, transportation and preparation for melting, while melting and slags superheating require additional energy, and the used slags are discharged into dumps, which are harmful for nature.

Due to the mentioned circumstances it is natural that the traditional processes of receiving metals including iron are focused on the handling of mono-ores which are rich in extracted metal. While using multimetal or low-metal content ore containing high-melting compounds of non-reducible metals, there appear difficulties with slags formation, the work of aggregates deteriorates and the technical and economic performances decrease.

Iron ore of Bakal deposit is easily reducible; it contains a little amount of harmful impurities, but in the blast-furnace practice it can be used only as an addition to other ores as it contains a lot of

(till 28 %) high-melting magnesium oxide. Till present the existing enrichment methods have not been able to decrease the content of magnesium oxide. It prevents application of Bakal siderite in a blast furnace.

In the recent years the authors have been developing theoretical principles and methods of selective reduction of iron in a crystal lattice of complex oxides, where iron is located in the lattice points together with isomorphic cations of magnesium, manganese, aluminum, chrome, titanium and other elements [1-8]. It is shown that the essence of reduction consists not in removing oxygen but in returning the electrons lost by the cations of oxidized metals, which are located close to oxygen ions in a lattice. That is why the record of reaction $\text{Me}^{2+} + 2\text{e} = \text{Me}$ conforms to the essence of reduction process; it reveals the electrochemical nature of the process, feasibility of spatial separation of metal reduction and a reducer oxidation reactions, feasibility of electric circuit closure between an oxidation agent and reducers by electrons flow, reduction of metals in the midst of oxygen anions, i.e. inside oxide where the reduction in a particular point inside the volume can take place without transfer of reagent therein. It allows extracting iron from the lattice of complex oxide without oxide melting.

2. PURPOSE

The purpose of the work consists in the research of iron extraction from the crystal lattice of complex oxide which is formed in the process of sideroplesite dissociation without oxide melting.

3. METHODS OF EXPERIMENTS

The subject of the research is sideroplesite of Bakal deposit. Lump ore of 15...25 mm size and ore powder of 0...500 micrometers size were used as a sample. Ore lumps were placed in a graphite pot and covered with a reducer. Ore powders were mixed with a reducer the quantity of which was higher than it is necessary for reduction and the prepared mixture was placed in a graphite pot. As a reducing agent there were used two carbon-containing materials possessing different reducing abilities – graphite powder and power-generating coal powder. While using coal the reduction could take place not only by solid carbon but by gas hydrocarbons as well, the yield of which makes up 41,6 % at the coal destruction.

The reduction was carried out in a hermetically-sealed Tamman furnace at the continuous heating with the rate of 10°C/min up to 900...1400°C and isothermal holding at the experimentally specified temperature. The temperature was measured with the help of Wolframium Rhenium-Wolframium thermocouple BP5/20 submerged into the reaction mixture. The time of holding varied from 30 minutes up to 4 hours.

The base ore and the samples after the reduction were used to produce samples for the X-ray phase analysis which was carried out at the X-ray diffraction meter DRON-4. For investigation of initial and reduced samples microstructure there were prepared polished sections. Chemical composition of phases was determined by the electron-probe method at the scanning electronic microscope JSM-6460LV of JEOL production.

4. RESULTS OF EXPERIMENTS

Siderite ore of Bakal deposit presents sedimentary rock formed by the layers of sideroplesite with the impregnation of quartz grains. Sideroplesite composition on average conforms to the formula $(\text{Fe}_{0.74}, \text{Mg}_{0.24}, \text{Mn}_{0.02})\text{CO}_3$ [9]. According to the results of the X-ray phase analysis the base sideroplesite contains such compounds as FeCO_3 , $(\text{Mg}, \text{Fe})\text{CO}_3$ and $\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$, where FeCO_3 and $(\text{Mg}, \text{Fe})\text{CO}_3$ are prevailing. After the dissociation of carbonates there are found oxides

(Fe,Mg,Mn)O and (Fe,Mg,Mn)O·Fe₂O₃ in the samples.

Experiments with lump ore and fines ore with different holding time and at different temperatures allowed tracing the development of a reduction process from the beginning till the complete reduction of iron ore. At the initial stage the metal reduction emerges in the interlayers between the oxide crystals (figure 1). At that, while using graphite or coal the emergence of metal evolutions is not correlated with the pores but with oxide phase grain boundaries. Further reduction comes amid the decrease of pores in size and their total disappearance. Final product of reduction process is a composite consisting of metallic iron and oxide residual.

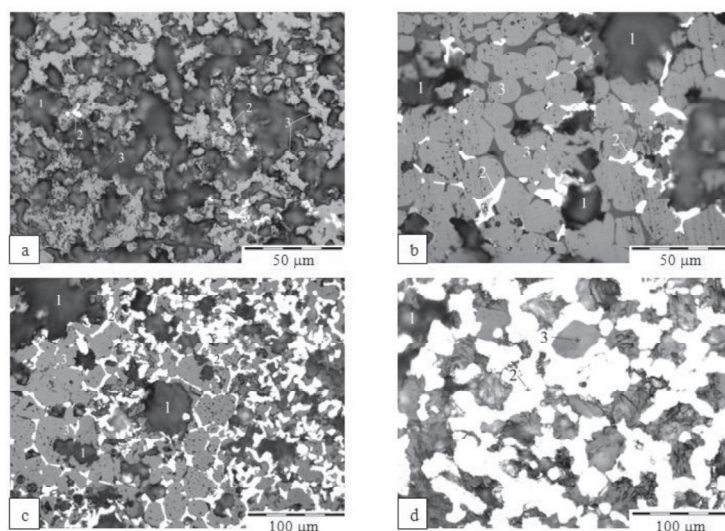


Figure 1: Consequence (a-d) of metallic phase in a porous piece of decomposed sideroplesite at the temperature of 1300°C and 1 hour holding: 1 – pores, 2 – metal, 3 – oxide

While using graphite as a reducing agent the reduction process developed practically in the bulk lump ore without distinct boundary between the initial oxide phase and a layer subjected to the reduction. Increase of holding time or temperature leads to practically total iron reduction in the whole piece. For example, at the temperature of 1200°C and holding time of 4 hours the reduction of former sideroplesite pieces took place in the whole volume and the remaining content of the iron atom in an oxide residue became equal to 6,2 atomic % (figure 2).

According to the data from X-ray phase analysis after the experiments the pieces contained metallic iron (with manganese impurity according to the data from electron-probe test) and silicate of (Mg_{1.145}Fe_{0.855})SiO₄ composition, as well as a little amount of FeO (table 1).

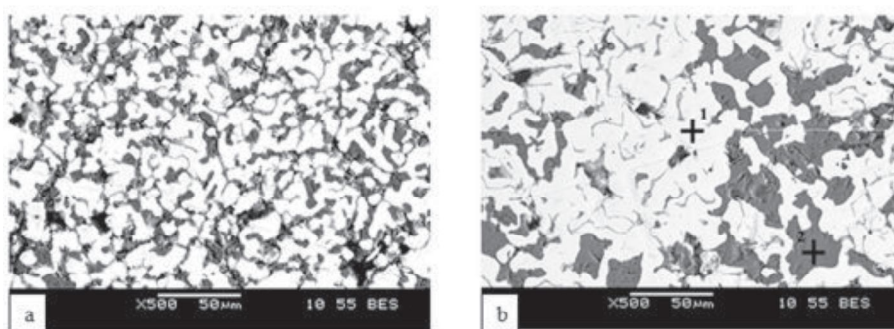


Figure 2: Result of iron lump reduction by graphite at the temperature of 1200°C and 4 hours holding

Content of elements in points, atomic %:

	O	Mg	Mn	Fe
1	0	0	0	100
2	37.66	44.59	11.54	6.20

Table 1: Composition of phases after the reducing roasting at the temperature of 1300°C and 3 hours holding

№	Sample		Fe [10]		FeO [11]		(Mg _{1,145} Fe _{0,855})SiO ₄ [12]	
	d	int.	d	int.	d	int.	d	int.
1	2,53	99					2,53	694
2	2,48	110			2,49	668	2,48	999
3	2,15	168			2,15	999		
4	2,03	778	2,03	100			2,04	35
5	1,76	118					1,76	608
6	1,52	81			1,52	458	1,52	44
7	1,49	80					1,49	262
8	1,43	111	1,43	20			1,45	42
9	1,17	314	1,17	30			1,17	7
10	0,91	209	0,91	12				

Using coal as a reducing agent came amid an evolution on the surface of layer, where the reduction process passed practically completely (figure 3). The boundary of this layer can be sufficiently distinctly seen through the optical microscope. At the experimental temperature of 900°C and 1100°C and 30 minutes holding the width of the layer varied from 0.5 up to 1 mm (fig. 3 a.). At the temperature of 1300°C the width of this layer reached 2 mm. The longer holding (2 hours) at 1300°C contributed to layer width increase, while the boundary between reduced and non-reduced material became less visible. The pores quantity and size considerably decreased.

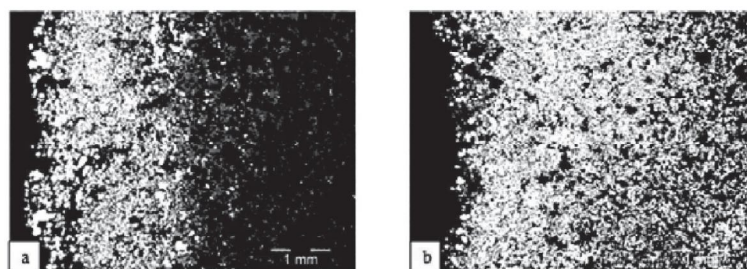


Figure 3: Layer of reduced iron in the former sideroplesite piece in the mixture with coal:
a) at the temperature of 1300°C and 60 minutes holding,
b) at the temperature of 1300°C and 120 minutes holding

Increase of temperature up to 1400°C led to the proportional separation of iron in the whole volume of ore lump.

Reduction of iron in fines ore in the mixture with graphite at the temperature of 1200°C and 60 minutes holding led to the mixture partial sintering, but the sinter could be easily grinded in hands. At that, the mixture contained both molten metal particles and particles of metal oxide composite (figure 4).

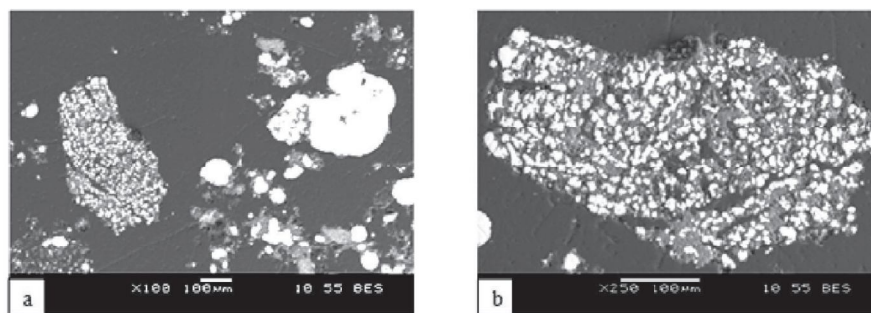


Figure 4: Result of iron fines ore reduction by graphite at the temperature of 1200°C and 1 hours holding: a) general view, b) metal oxide composite

By means of X-ray phase analysis it is discovered that the samples of powder, obtained in the result of ore powders and graphite mixture sintering, contain metallic iron, iron carbide Fe_3C , iron carbide with a little quantity of manganese impurity ($\text{Fe}_{2.7}\text{Mn}_{0.3}\text{C}_3$). Magnesium is discovered in the form of magnesiowustite, the composition of which conforms to the formula $(\text{MgO})_{0.91}(\text{FeO})_{0.09}$ (table 2).

Table 2: Composition of phases after the reducing roasting at the temperature of 1200°C and 1 hours holding

№	Sample		Fe [10]		Fe_3C [13]		$\text{Fe}_{2.7}\text{Mn}_{0.3}\text{C}_3$ [14]		$(\text{MgO})_{0.91}(\text{FeO})_{0.09}$ [15]	
	d	int.	d	int.	d	int.	d	int.	d	int.
1	2,43	22,9			2,42	10			2,44	166
2	2,39	21,4					2,38	306		
3	2,11	142			2,11	34			2,11	999
4	2,07	33			2,08	66	2,06	578		
5	2,03	210	2,03	100	2,03	26	2,01	999		
6	1,49	72,7							1,49	448
7	1,43	31,4	1,43	20						
8	1,22	40,9					1,22	128	1,22	110

While using coal instead of graphite the form of particles has changed. Most of particles received a cover from metallic iron on the surface (figure 5).

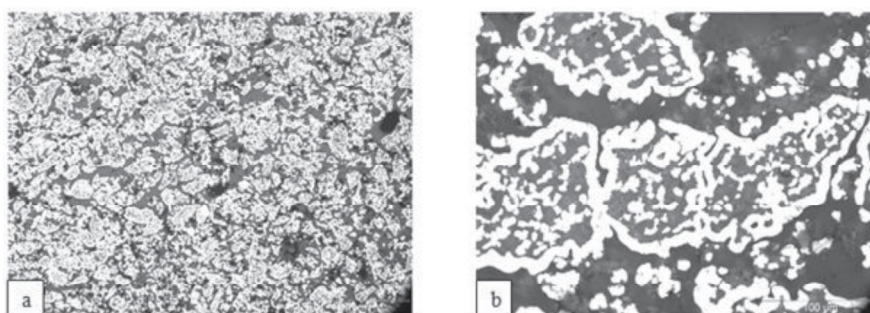


Figure 5: Result of iron reduction in the former sideroplesite powder in the mixture with coal: a) general view of particles, b) zoomed structure of particles

5. DISCUSSION OF THE RESULTS

The process of iron reduction is preceded by the process of sideroplesite decomposition. According to the data received by means of synchronous thermal analysis device **STA449C Jupiter**, the process of dissociation takes place at the temperature of 350...700°C in 2 stages [16]. In consequence of the evolution of gas decomposition products CO₂ and CO (mass loss makes up 32 %) complex oxides (Fe,Mg,Mn)O and (Fe,Mg,Mn)O·Fe₂O₃ and a great number of pores appear in a lump of ore. At further increase of temperature iron reduces from the complex oxides.

Experimental application of lumpy ores gave a chance to trace different reduction stages at the transverse section of one sample, as the reduction starts from the surface and consequently develops inside a sample. The received results show that the reduction process develops not only on the surface of reducing agent and oxide contact, but in bulk complex oxide, what proves reduction electrochemical mechanism.

The obtained results allow assessing impact of temperature and holding time on development of reduction process in lumpy ore and in powdered ore, in mixture of ore material with graphite or coal. While using graphite the analysis reveals metallic iron and silicate of (Mg_{1,145}Fe_{0,855})SiO₄ composition, as well as a little quantity of iron monoxide FeO. Iron in the samples from the mixture of ore powders and graphite at the experimental temperature of 1200°C and 1 hour of holding exists in the form of pure iron and in the form of carbide Fe₃C, sometimes with a little quantity of manganese in the form of carbide (Fe_{2,7}Mn_{0,3})C₃. Carbon penetration in iron is apparently connected with a great surface of ore particles and a reducing agent contact as well as sufficient superabundance of a reducing agent. Correlation of iron and its carbides highs intensity at X-ray diagrams is about the same, what proves carbon penetration just in a certain part of the reduced iron. Apparently, carbon did not penetrate into iron inside the particles.

The experiments on iron reduction in ore lump by coal show the same consequence of the reduction process as in experiments with graphite. In the meanwhile at the reduction by coal the surfaces of pieces and, particularly, of powdered ore particles show a denser layer of the reduced iron which acquires the form of continuous cover on the surface of small particles (Figure 5). Apparently, such difference in the character of the reduced iron distribution is dependent on different intensity of oxygen anions extraction by graphite carbon and carbon-containing coal components. Coal contains about 40% (by mass) of volatile hydrocarbons, which can be more active reducers in comparison with graphite carbon [17].

Earlier [6] it was theoretically proven that in the conditions when the rate of anion vacancies formation under the influence of a strong reducing agent exceeds the rate of their diffusion in the bulk oxide, the reduced metal forms on the surface, and when the rate of vacancies diffusion exceeds the rate of their formation, the reduced metal appears in the bulk crystal lattice in its defects.

6. CONCLUSION

1. Electrochemical mechanism of metals reduction is proven.
2. Feasibility of iron selective reduction in a crystal lattice of complex iron-manganese-magnesium oxide without oxide melting is shown.
3. Application of reducing agents with different oxygen affinity can change the correlation of the rate of anion vacancies formation on the surface of reagents interaction and the rate of vacancies diffusion in the bulk oxide, what causes changes in the character of the reduced metal separation.
4. At relatively low rate of anion vacancies formation at the usage of a weak reducing agent and high rate of their diffusion in view of intensive thermal motion the reduced metal separates out in the bulk oxide; at inverse correlation of rates the metal forms a cover on the surface of oxide.

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