A study on the production processes of granulated iron

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Abstract. The results of theoretical and experimental studies on the production process of high-quality granulated iron using hematite-magnetite iron ore and coal of different brands as a raw material are presented. According to the research the optimal coal consumption, temperature and time parameters of the metallization process, necessary for obtaining metallized materials with the specified composition and metallization degree, are defined. The conditions for the formation of metal granules with high content (over 98%) of primary iron are found. The process includes two stages: initially the solid-phase reduction of iron from oxides with production of metallized sponge material is carried out, further as the temperature increases the separation of slag and metal phases takes place.

1. Introduction
Most modern steel grades have rigid restrictions on the content of non-ferrous metal impurities. In addition, in the initial raw material – metal scrap the impurities content is growing steadily (Figure 1), and to date there are no effective methods for their removal from the melt. In this regard, production and application of metallized materials, which do not contain non-ferrous metals and can replace metallic scrap, has become a perspective direction. Production volumes of metallized raw materials are steadily growing. [1] Currently, most metallized materials are produced with the use of converted gas as a reducing agent, but a faster rate has the developing technology of metallized material production using a solid carbonaceous component as a reductant [2]. The most progressive way of advanced processing of iron ore materials with coal is the production of granulated iron [3].
The granulated iron (Figure 2) is a new kind of metallurgical raw material significantly improving the quality of material metal products and reducing production costs. Production technologies of granulated iron are called “third-generation of iron production” [4]. The objective of the conducted research was to study the process of obtaining the granulated iron using iron ores and coals from Kemerovo region.

At present there are several technologies for the production of granulated iron. According to the patent of the company “Kobe Steel – ITmkS” (Japan), metallic iron is produced by direct reduction of material containing iron oxides, using a solid carbon-containing reductant. The charge is fed into a rotary furnace, where at the beginning in the direction of hearth movement, the solid-phase restoration occurs, and in the end of hearth travel carbonization and melting take place. Between the solid reduction zone and the zone of carburization and melting there is a zone of reduction with the adjustable within the range 1473-1773 K. Another way to obtain granulated metallic iron is the feeding of ore smelting mixture into the rotary furnace where initially the solid phase reduction of iron from oxides takes place with subsequent melting and separation of slag from metallic granules. The quantity of CaO, MgO and SiO₂, contained in the charge mixture is adjusted in such a way that a slag,
having a basicity from 1.3 to 2.3, is formed (the basicity is calculated according to the ratio – (CaO + MgO)/SiO$_2$). The content of MgO in the slag should be in the range from 5 to 13%, which provides a reduced sulfur content in the granulated iron [5].

The appearance of a liquid phase promotes the formation of large granules. Formed as a result of reduction particles of metallic iron are quickly carbonized due to the excess of carbon reductant in the material mixture. As a result of carburization the temperature of their melting is rapidly reduced, which ensures the concentration of reduced iron fine particles in the form of coarse granules.

The authors [6] developed schemes for metal production in the liquid state. These schemes involve a preliminary reduction of iron from ores or concentrates by gaseous or solid reducing agents in the rotary furnaces, furnaces with a suspended layer or other units, and a subsequent separating smelting in the rotary or electric furnaces. Selectivity of reduction is realized at the first stage of the process at moderate temperatures; stage of separating smelting is carried out in the manner so that the reduction processes would not further develop. Schemes, involving the iron extraction from complex ore in the solid state, presuppose production of metallized concentrates on the basis of solid-phase reduction of metal from oxides. The subsequent processing is carried out at temperatures of 1473-1623 K, the conditions are created for the development of coagulation of metal grains. One of the alternative schemes of metallized materials production is the method of pellets production in which metal is coagulated inside the slag shell.

As appears from the described methods the granulated iron is the product of the liquid phase separation of metallization products. Initially a solid-phase reduction of iron from oxides is carried out; as a result of temperature increase the separation of solid-phase reduction products takes place. Thus, the granulated iron is formed by macroscopic, visible separation of metal and slag. To ensure the conditions for separation of metal and slag phases it is necessary for one of the phases (metal or slag) to be liquid, and the rapid formation of a fluid phase occurs as temperatures go up.

2. Theoretical research
Thermodynamic modelling of solid-phase reduction of iron from oxides with use of different coal brands as reducing agents showed that in the result of interaction of FeO, SiO$_2$, Al$_2$O$_3$, CaO during solid-phase reduction of iron from iron ore oxides in the ranges of the studied temperatures, the formation of compounds shown in Table 1 is possible.

| Mineral          | Formula                          | Name          | Melting temperature, K |
|------------------|----------------------------------|---------------|------------------------|
| Iron silicates   | (CaO)$_{0.5}$,(FeO)$_{1.5}$,SiO$_2$ | –             | 1403                   |
| (CaO)$_{0.5}$(FeO)$_{2}$ | CaO·FeO·SiO$_2$                  | –             | 1483                   |
| SiO$_2$         | FeO·SiO$_2$                      | Fayalite      | 1478                   |
| Calcium ferrites | CaO·2Fe$_2$O$_3$                 | Semicalcium   | 1503                   |
|                  | 2CaO·Fe$_2$O$_3$                 | Dicalcium     | 1709                   |
|                  | CaO·Fe$_2$O$_3$                  | Monocalcium   | 1489                   |
| Calcium silicates | CaO·SiO$_2$                     | Wollastonite  | 1813                   |
|                  | 3CaO·2SiO$_2$                   | Rankinite     | 1748                   |

*the indicated minerals can form eutectics that melt at lower temperatures

It is known [1] that the formation of primary fluid phases is preceded by interaction between SiO$_2$ and FeO. It should be borne in mind that the mass fraction of FeO changes in the course of the reduction processes, and the system is heterogeneous. The most low-melting compound of these oxides are minerals from olivine group. Probably, the main role in the formation of the initial slag phase belongs to iron silicates, namely fayalite. According to the known data about the temperatures
of the beginning of chemical interaction between the solid phases, the temperature of the beginning of fayalite formation during heating in the presence of just reduced iron is 1263 K.

With the help of software package FactSage 6.4 the analysis of interaction between $\text{SiO}_2$ and FeO with change in molar concentrations and temperatures was performed. In the diagram FeO-Fe$_2$O$_3$-SiO$_2$ (Figure 3) the zone of iron silicates formation at temperatures 1373 K and 1573 K is established. The analysis of the received data allowed us to determine the boundary zones of concentrations FeO and SiO$_2$ favorable for the formation of low-melting phases at different temperatures [7].

![Figure 3. Diagram FeO-Fe$_2$O$_3$-SiO$_2$ at temperatures 1373 K (a) and 1573 K (b).](image)

The results of calculations, performed using the software complex “TERRA” for materials in our experimental studies (Table 2, 3), allowed us to establish the optimum ratios of components in the ore-coal mixtures needed for the production of metallized products with the given composition [8, 9].

3. Experimental research
The task of experimental studies consisted in production of granulated iron using coal as a reducing agent, determination of conditions for formation of liquid phases and coagulation of metal droplets on the basis of theoretical studies.

For the experiments ore-coal briquettes of various compositions were produced. As an iron component ores from Kemerovo region were used. As solid carbonaceous reductants coals of different technological marks were applied. Composition of iron ores and reducing agents characteristics are shown in Tables 2 and 3.

| Chemical composition of iron ore ZhR-1, % mass |
|---------------------------------------------|
| Fe$_{\text{tot}}$ | SiO$_2$ | Al$_2$O$_3$ | P$_2$O$_5$ | CaO | MgO | S | moisture |
| 44.19 | 13.74 | 3.99 | 0.117 | 9.63 | 2.29 | 2.65 | 6.3 |

| Chemical composition of iron ore ZhR-2, % mass |
|---------------------------------------------|
| Fe$_{\text{tot}}$ | SiO$_2$ | Al$_2$O$_3$ | P$_2$O$_5$ | CaO | MgO | S | moisture |
| 52.3 | 19.15 | 3.31 | 0.072 | 0.94 | 0.76 | 0.42 | 5.78 |

| Chemical composition of iron ore ZhR-3, % mass |
|---------------------------------------------|
| Fe$_{\text{tot}}$ | SiO$_2$ | Al$_2$O$_3$ | P$_2$O$_5$ | CaO | MgO | S | moisture |
| 61.2 | 6.75 | 2.2 | 0.02 | 1.96 | 2.31 | 0.41 | 7.2 |
The components ratio in the mixture was determined according to the thermodynamic calculations. Experiments were performed on the basis of the developed techniques of solid-phase reduction of iron from oxides with the use of solid carbonaceous reducing agents [10]. The metallization was performed by reductive roasting of ore-coal briquettes in the laboratory furnace at temperature 1273 K for 40 min. The metallization mode was selected based on previous studies. Spongy metalized materials were produced.

The study on the liquid phase separation of products of solid phase metallization was carried out by stepwise increase of the temperature within the range 1273-1673 K and analysis of the obtained melt products. Isothermal exposure at each temperature was 10 minutes. These materials were studied by chemical, spectral, X-ray diffraction analysis.

4. Results and discussion
The results of experiments determined that by changing the composition of the initial ore-coal mixture, temperature and time of reduction roasting metallized materials can be obtained with a specified amount $F_{\text{met}}$, FeO and SiO$_2$. The results of melt separation (Table 4) for metallized materials with a high degree of metallization (over 95%) showed that the formation process of fluid phases and coagulation of metal droplets occurs less intensively at higher temperatures than for metallized materials with a lower (less than 95%) degree of metallization. It is found that when using coals of various technological grades as reducing agents the coagulation of metal granules takes place differently, probably due to the influence of different compositions of reducing ash.

| Table 3. Characteristics of reducing agents. |
|---------------------------------------------|
| Characteristic                              | Coal grade       |
|                                             | Lignite B2 | Long-flame | Low-caking | Lean coal |
| $C_{\text{i,fix}}$ (content of the fixed carbon), % | 49.1  | 55.6 | 70.2 | 76.3 |
| $V^0$ (volatile yield on the working mass), % | 42.1  | 36.0 | 20.6 | 9.34 |
| $W^p$ (moisture on the working mass), %     | 24.7  | 10.4 | 6.7  | 5.1  |
| $A^1$ (ash on the dry basis), %             | 7.83  | 5.64 | 6.41 | 8.34 |

Chemical composition of ash, %:
- Fe$_2$O$_3$
- Al$_2$O$_3$
- CaO
- MgO
- P$_2$O$_5$
- SiO$_2$
- S
- Apparent density, $\gamma_{\text{af}}$, g/cm$^3$
- Real density, $\gamma_{\text{f}}$, g/cm$^3$
- Porosity, P, %
- Reactivity on CO$_2$ at 1000 °C, K, cm$^3$/g·s

Elemental composition, %:
- $C^\text{daf}$ (carbon content on dry ash-free basis), %
- $H^\text{daf}$ (hydrogen content on a dry ash-free basis), %
- $N^\text{daf}$ (nitrogen content on dry ash-free basis), %
- $O^\text{daf}$ (oxygen content on a dry ash-free basis), %
- $S^\text{daf}$ (sulfur content in the dry ash-free basis), %

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| Table 4. Results of the experiment. |
|-------------------------------------|
| Characteristic                      | Value |
|-------------------------------------|-------|
| $F_{\text{met}}$                   | 90    |
| FeO                                | 4.48  |
| SiO$_2$                            | 4.48  |
| $\gamma_{\text{af}}$               | 1.15  |
| $\gamma_{\text{f}}$                | 1.20  |
| P                                   | 1.28  |
| Reactivity on CO$_2$ at 1000 °C, K, cm$^3$/g·s | 1.28  |
Reducing agent | Granule formation temperature (> 1 mm), K | Mass of the granulated iron*, g | Spectral analysis of the granules
---|---|---|---
Lignite | 1573 | 412 | Fe_{met}> 99 %; 
Long-flame coal | 1573 | 402 | C < 1 %; 
Low-caking coal | 1623 | 420 | Si < 0.5 %; Al < 0.5 %; 
Lean coal | 1673 | 415 | P < 0.1 %; S < 0.1 %

*amount of iron obtained by using 1 kg of iron ore (ZhR-2).

The spectral analysis of the obtained granules showed a high content of primary ore and low content of residual elements in the granules. Metal composition is determined by the process parameters and depends on the composition of iron ore and the used reducing agent. The lowest temperature of the beginning formation of visible, larger than 1 mm, metal granules was 1473 K for the mixture with brown coal as a reductant.

5. Conclusions
The results of the research theoretically proved and experimentally confirmed the possibility of obtaining high-quality granulated iron using iron ores and coals from Kemerovo region as raw materials. It was found that the process includes two stages. Initially the solid-phase reduction of iron from oxides is performed obtaining metallized sponge material, then as temperature increases the separation of slag and metal phases occurs.

6. References
[1] Yusfin Yu S and Pashkov N F 2007 Metallurgy of Iron (M.: IKTs “Akademkniga”) p 464
[2] Naito M 2006 Shinmittetsu Giho 384 2
[3] Zhang Y Y et al 2013 Advanced Materials Research 746 533–538
[4] Nagano K I 2004 Tetsu-to-Hagane 90 (2) 51–60
[5] Seki K and Tanaka H 2008 Changes in Paradigm Development of Iron & Steel Industry by Applying Coal Based Processes: FASTMELT® & imtk3® (Tokyo Kobe Steel Ltd)
[6] Tsuge Osamu and Ito Suzo Method of Production of Granulated Iron Patent No. 2301834
[7] Bale C W et al 2013 Thermfact and GTT-Technologies
[8] Nokhrina O I, Rozhihina I D, Proshunin I E, Hodosov I E and Osipova V G 2015 Applied Mechanics and Materials 770 8–13
[9] Nokhrina O I, Rozhihina I D, Proshunin I E and Hodosov I E 2015 Steel in Translation 45 (5) 295–300
[10] Nokhrina O I, Rozhihina I D and Hodosov I E 2015 IOP Conference Series: Materials Science and Engineering (IOP Publishing) 9 (1) 012045

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