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(54) **METHOD OF PRODUCING REDUCING AGENT FOR MANUFACTURING INDUSTRIAL SILICON**

(57) The invention relates to the field of metallurgy, particularly to techniques for producing reducing agents for manufacturing high-quality industrial silicon. A method of processing a carbon-containing feedstock to produce a reducing agent for manufacturing industrial silicon, includes heat treating a carbon-containing feedstock in a fluidized bed at a temperature of 700-850°C by blasting at high speeds with a mixture of air and water vapor to provide for the transition of iron-containing compounds in the carbon-containing feedstock to a magnetic form; cooling the resulting reducing agent; and then magnetically separating same over the course of 100-120 hours, immediately after the cooling stage, at a magnetic field induction magnitude of at least 1.1 T. The technical result consists in lowering the iron content of the reducing agent for manufacturing high-quality industrial silicon.

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## Description

**[0001]** The invention relates to the field of metallurgy, in particular, to techniques for producing reducing agents for manufacturing superpurity industrial silicon.

**[0002]** A method of silicon manufacturing is known that includes dosing, mixing, loading, and melting a fusion mixture comprising quartzite and charcoal, in an electric furnace (Ragulina R. I., Yemlin B. N. Elektrotermiya Kremniya i Silumina (Electrothermy of Silicon and Silumin). Moscow: Metallurgiya, 1972, p. 240). However, this manufacturing method involves the consumption of charcoal, an extremely scarce and expensive raw material. Furthermore, this method entails exceptionally high losses of a reducing agent due to the very low strength of charcoal, which heavily crushes and grinds when introduced into the fusion mixture, and especially when the fusion mixture is reloaded.

**[0003]** A method of silicon manufacturing is known that includes dosing, mixing, loading, and melting a fusion mixture comprising quartzite and Columbian coals with very low iron and ash content, in an electric furnace ([http://www.up-pro.ru/library/production\\_management/systems/kremnij-kruchkov.html](http://www.up-pro.ru/library/production_management/systems/kremnij-kruchkov.html)). The drawback of this method is the high cost of Columbian coals due to transportation expenses.

**[0004]** A method of producing a briquetted mix for silicon manufacturing is known (patent RU 2528666, C01B33/025, Publ. 05.27.2014), which includes mixing a silica-containing raw material and a carbonaceous material of plant origin (sawdust, wood waste, etc.) and briquetting them to produce briquettes, which are subjected to thermal pyrolysis in the absence of oxygen until the pyrolysis gas is completely released. The drawbacks of this method are low strength, low bound carbon content, and high cost of briquette production.

**[0005]** A method of producing carbonizate (Rexyl) (patent KZ 23615, C10B57/00, C10B55/00, Publ. 12.15.2010) from non-caking bituminous coals is known, in which the coals are subjected to high temperature heat treatment in an inert atmosphere in the absence of air. The drawback of this method is the need to select raw materials for carbonizate production, more specifically, low-ash bituminous coals with a low content of detrimental impurities that all end up in the carbonizate after the heat treatment.

**[0006]** A method of producing a fusion mixture for melting pure silicon is known (patent RU 2424341, C22C33/04, C01B33/025, Publ. 07.20.2011), wherein amorphous silicon dioxide is mixed with a carbon-containing reducing agent in the form of carbon black at a ratio of 1:1.5 and silica gel, followed by the fabrication of pellets or briquettes of various shapes that are dried and calcined at 900-1,200°C. The drawbacks of this method of fusion mixture production include the high cost of carbon black and an increased yield of volatile silicon monoxide SiO.

**[0007]** A method of briquetting semi-coke, primarily lignite, is known (patent RU 2376342, C10L5/12, Publ. 12.20.2009), comprising the following stages of preparing starting components: crushing semi-coke down to 0-7 mm, mixing semi-coke with hydrated lime with a water-to-lime ratio of 3:1 or 5:1, compressing, impregnating the briquettes with liquid glass, and drying.

**[0008]** The drawback of this method is a high ash and undesirable impurity content, in particular, iron content, which limits the application of the briquetted reducing agents in manufacturing premium grades of industrial silicon.

**[0009]** A method is known that includes heat treatment of a coal bed in a vertical shaft unit with firing at the side opposite the air supply. A coal fraction of 20-70 mm is used as a raw material, and air is supplied through the coal bed at a specific flow rate of 70-99.5 m<sup>3</sup>/(m<sup>2</sup>·h) depending on the coal grade. The method provides a solid product with higher strength, lower ash, as well as larger mean piece size, with a simultaneous increase in product yield (patent RU 2275407, C10B49/02, C10B53/00, Publ. 04.27.2006).

**[0010]** The drawback of the known technical solution is the presence of a mineral part in large pieces of the heat treated coal, contaminating the final product and limiting its application in silicon manufacturing.

**[0011]** A method of producing semi-coke is known, which includes the stages of heating, drying, and carbonizing solid carbon-containing feedstock with air blasting supplemented with a flammable gas having the temperature of exit from the unit and at a concentration not exceeding the lower flammability limit of the gas. The amount of supplemented gas is preferably 8-10% of the volume of the produced flammable gas. The carbonization temperature is 920-950°C. The technical result is improved semi-coke quality due to a reduced yield of volatiles in the product, increased semi-coke yield by about 5-6%, and shortened treatment duration (patent RU 2169166, C10B49/04, Publ. 06.20.2001).

**[0012]** The drawback of the analog is the presence of iron compounds in the mineral part, which deteriorates the quality of the produced industrial silicon.

**[0013]** The closest method in terms of technical essence is a method of processing coal crushed down to 10 mm, which is implemented by simultaneous thermal oxidative coal treatment at a temperature of 700-950°C due to partial coal oxidation with air and separation of the mineral part of the coal that is heavier than the coal. The blasting air for bed fluidization is supplied at a rate of 2,500-4,200 m<sup>3</sup>/(m<sup>2</sup>·h). Fine carbon, vapor gases from coal thermal decomposition, and coke gasification products partially burn in the fluidized bed, maintaining its working temperature. The heavier rock particles settle down in the lower part of the fluidized bed and are removed from the unit via a sifting grate. The combustion products are fed to the waste-heat boiler to generate thermal energy. The invention provides high-energy, low-ash, heat treated solid fuel from high-ash coals without preliminary upgrading of starting coal (patent RU2401295, C10B49/10,

Publ. 10.10.2010).

**[0014]** The drawback of the prototype is the insufficient coal separation from rock particles and high iron content, which limits the application of the briquetted reducing agents in manufacturing premium grades of industrial silicon.

**[0015]** The objective of the provided technical solution is to create a method of producing a reducing agent for silicon manufacturing, capable of substituting scarce and expensive reducing agents utilized in manufacturing high quality silicon.

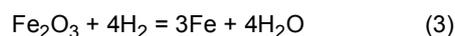
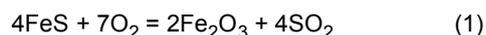
**[0016]** The technical result of the invention is lower iron content in the reducing agent for manufacturing high quality industrial silicon.

**[0017]** Said technical result is provided by the fact that the method of processing carbon-containing feedstock to produce a reducing agent for manufacturing industrial silicon includes heat treating a carbon-containing feedstock in a fluidized bed at a temperature of 700-850°C by blasting at high speeds with a mixture of air and water vapor to provide for the transition of iron-containing compounds in the carbon-containing feedstock to a magnetic form; cooling the resulting reducing agent; and then magnetically separating same over the course of 100-120 hours, immediately after the cooling stage, at a magnetic field induction of at least 1.1 T.

**[0018]** The lower the content of the mineral part in the starting coals and its iron concentration, the more likely the product is to have a low iron content. Therefore, utilization of low-ash, low-iron (not higher than 5%), inexpensive lignite coals is beneficial for the said technical result.

**[0019]** The starting carbon-containing feedstock contains iron primarily in the form of pyrite, marcasite, siderite, and hematite. In light fractions, iron is represented by hydroxides within clay minerals. When processing lignite coals into semi-coke, said mineral compounds pass into the final material and undergo phase transitions, depending on the conditions of the occurring redox processes at high temperatures.

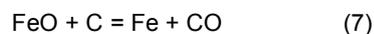
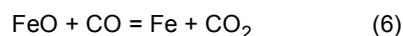
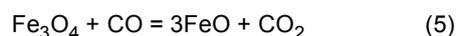
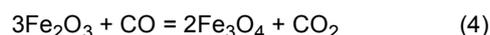
**[0020]** Thus, pyrite (marcasite) FeS<sub>2</sub>-iron disulfide, present in the starting coal, decomposes upon heating into iron sulfide and sulfur. The following reactions occur upon heating iron sulfide in oxygen:



**[0021]** Siderite (spathic iron ore) contains iron primarily in the form of carbonate (FeCO<sub>3</sub>). Under high temperatures, the carbon dioxide being eliminated renders the material porous, while easing its reduction.

**[0022]** Hematite and magnetite (Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>). The reduction of hematite and magnetite upon heating with carbon produces fine-crystalline iron oxide that readily transforms into Fe. The zone of transition from FeO to Fe practically merges with the Fe<sub>3</sub>O<sub>4</sub>-FeO zone. It has been found that the reaction rates of Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-FeO at 700-750°C are rather close.

**[0023]** The process of reduction of iron oxides:



**[0024]** The process of iron reduction from oxides proceeds step-wise by sequential transition, from higher to lower oxides, according to the following scheme: Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-FeO-Fe (above 570°C) or Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>-Fe (below 570°C). Upon low-temperature reduction of hematite (<800°C), magnetite, as an intermediate oxide stage, has a noticeably different composition than stoichiometric. An analysis of the reduction products has demonstrated that there is an entire set of magnetites with varying stoichiometry. The appearance of nonstoichiometric magnetite at low temperatures and its absence at high temperatures of hematite reduction confirm the presence of the limiting influence of solid-phase processes in reduction products.

**[0025]** The reduction rate depends on the nature of the oxide and the nature and properties of the reducing agent, which can be, for example, lignite coal and its derivatives (semi-coke). Thus, an avalanche increase in the reduction rate is observed when good contact of oxides with semi-coke carbon is ensured. Therefore, when using semi-coke formed in the process of lignite coal carbonization, the efficiency of the process, as for any solid-phase reaction, will depend on the contact between the semi-coke and the oxide being reduced, which is locked with carbon. The reduction process is also affected by the reactivity of lignite coal semi-coke and its content of volatile components. Any lignite coal

may be used as the carbon-containing feedstock to produce the reducing agent. However, the most promising one is lignite coal from the Kansk-Achinsk basin due to the large reserves (the predicted resources being 309.9 billion tons, or 23.4% of Russian coal resources), low ash (3.4-22.3%) and insignificant iron content.

**[0026]** It is known that magnetic separation is most efficient for materials containing iron impurities in the form of magnetite  $\text{Fe}_3\text{O}_4$ , which has strong magnetic properties. In the provided technical solution, the reactions of reducing iron oxides to magnetite (and/or any other magnetic form of the processed carbon-containing feedstock) proceed upon heating the carbon-containing feedstock, such as lignite coal, in a fluidized bed at 700-850°C to form the reducing agent (semi-coke), which has, in aggregate, the following properties (composition, wt.%):

- Ash ( $A^d$ ): 5.0-8.0%;
- $\text{Fe}_2\text{O}_3$  content in ash: 0.8-1.2%;
- Volatiles ( $V^{daf}$ ): 13.0-15.5%;
- Bound carbon (C): 75.0-80.0%;
- Reactivity: at least  $8.1 \text{ cm}^3/(\text{g}\cdot\text{s})$ ;
- Specific electrical resistivity: at least  $1.37 \times 10^3 \text{ Ohm}\cdot\text{cm}$ ;
- Specific area: 120-500  $\text{m}^2/\text{g}$ .

**[0027]** The method is implemented as follows. Carbon-containing feedstock (lignite coal) having a size of up to 10 mm is supplied with a screw to a gas distributor plate. The coal is subjected to heat treatment (semi-coking) in a fluidized bed at a temperature of 700-850°C. Coal fluidization is achieved using a mixture of air and water vapor supplied under the gas distributor plate. The water vapor supply under the plate prevents its clinkering in case of thermal abuse.

**[0028]** The particles of the starting coal supplied to the lower part of the fluidized bed experience high-speed heating, releasing water and resin vapors, as well as decomposition gases in the process. Each coal particle is surrounded by a cloud of protective atmosphere, blocking air oxygen access to its surface. Combustion of the evolving gases and vapors occurs at the periphery of the gas cloud. Thus, in the lower part of the fluidized bed, the surface of coal particles is not subjected to ashing by air oxygen, which ensures the required content level of the reducing carbon (yield).

**[0029]** High-speed heating is accompanied by intense grinding of coal particles as a result of their thermal destruction and crushing in collisions. It also ensures good contact of iron oxides with carbon, providing high rates of their reduction and transition of iron compounds in the carbon-containing feedstock to magnetic forms.

**[0030]** Particle grinding is accompanied by a decrease in their apparent density due to the release of water and resin vapors from the particle pores. Therefore, the finer and lighter particles of the formed semi-coke move to the upper part of the fluidized bed, where the semi-coking continues, accompanied by the release of decomposition gases and resin vapors, but not as vigorously as in the lower part of the fluidized bed.

**[0031]** While in the lower part of the fluidized bed, the coal particles are in a vapor air medium with substantial oxygen content, and the gas medium in the upper part consists of combustion products with the admixture of semi-coking gas. The oxygen content in this medium is not high, and thus no ashing of the surface of the forming semi-coke particles occurs.

**[0032]** In the upper part of the fluidized bed, water vapors induce semi-coke activation, increasing the semi-coke surface and enhancing its reactivity in chemical reactions.

**[0033]** Along with the coal, the rock and locked coal settle in the lower part of the fluidized bed, where due to their higher density, they are removed from the fluidized bed onto the gas distribution plate and are periodically unloaded from it.

**[0034]** The low-energy gas exiting the fluidized bed is passed to the separation space of the unit. Large semi-coke particles carried from the bed settle back into the fluidized bed, while the gas exits the unit to be stripped from semi-coke fines in a cyclone. The semi-coke fines are added to the semi-coke unloaded from the unit, and the forming low-energy gas is burned in the furnace of the waste-heat boiler.

**[0035]** The subsequent magnetic separation in the separator lowers the iron content to acceptable levels, ensuring high quality of the reducing agent.

**[0036]** Example 1. The reducing agent was produced using lignite coal of the Berezovskoe deposit supplied to the fluidized bed boiler. The material was processed in different temperature intervals: 550-700, 700-850, and above 850°C. At temperatures of 550-700°C, the produced reducing agent (semi-coke) had insufficient pyrolysis, high content of volatiles, and low magnetic susceptibility.

**[0037]** At temperatures above 850°C, the yield was reduced. Therefore, the 700-850°C temperature range is optimal.

**[0038]** Experiments have demonstrated that prolonged storage of the pyrolyzed lignite coal semi-coke resulted in lower efficiency of subsequent separation of the iron-containing magnetic fraction from the lignite coal semi-coke.

**[0039]** Example 2. The maximum decrease of the iron content in the carbon material (down to 0.11 wt.%) after passing it through a magnetic separator was observed immediately after the pyrolysis. After 5 days, the iron separation efficiency dropped to 0.15 wt.%. When separating the pyrolyzed product with a storage time of less than 100 hours, the efficiency

of iron separation was less than 0.11 wt.%.

**[0040]** The efficiency of iron extraction depended on the magnetic field induction magnitude. There is an optimum level of magnetic field induction magnitude, below which the efficiency of separating the magnetic fractions decreases. Excessively high magnetic field induction is economically impractical since the equipment cost rises. Low magnetic field induction magnitude results in increased iron content in the magnetically treated reducing agent.

**[0041]** Example 3. The produced reducing agent was separated in a magnetic field. For magnetic field induction magnitude higher than 1.1 T, the iron content in the magnetically treated semi-coke reached 0.11 wt.%. At a lower magnetic field induction magnitude (0.8 T), iron content amounted to 0.2 wt.%.

### Claims

1. A method of processing carbon-containing feedstock to produce a reducing agent for manufacturing industrial silicon, which includes heat treating a carbon-containing feedstock in a fluidized bed at a temperature of 700-850°C by blasting at high speeds with a mixture of air and water vapor to provide for the transition of iron-containing compounds in the carbon-containing feedstock to a magnetic form; cooling the resulting reducing agent; and then magnetically separating same over the course of 100-120 hours, immediately after the cooling stage, at a magnetic field induction magnitude of at least 1.1 T.
2. The method of claim 1, **characterized in that** the lignite coal with an iron content in the ash of not more than 5% is used as the carbon-containing feedstock.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/RU 2018/050136

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A. CLASSIFICATION OF SUBJECT MATTER  
C10B 49/10 (2006.01); C10B 53/04 (2006.01)  
According to International Patent Classification (IPC) or to both national classification and IPC

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B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
PatSearch (RUPTO internal), USPTO, PAJ, K-PION, Esp@cenet

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2401295 C1 (ISLAMOV S.R.) 10.10.2010, the abstract	1-2
A	RU 2073061 C1 (MERTS R.KH.) 10.02.1997, the abstract	1-2
A	RU 2285715 C1 (OOO «SIBTERMO») 20.10.2006, the claims, example 3	1-2
A	US 4052170 A (MOBIL OIL CORPORATION) 04.10.1997, the abstract	1-2

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Further documents are listed in the continuation of Box C.  See patent family annex.

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\* Special categories of cited documents:  
 "A" document defining the general state of the art which is not considered to be of particular relevance  
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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
 "&" document member of the same patent family

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Date of the actual completion of the international search 30 January 2019 (30.01.2019)	Date of mailing of the international search report 07 February 2019 (07.02.2019)
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**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- RU 2528666 [0004]
- KZ 23615 [0005]
- RU 2424341 [0006]
- RU 2376342 [0007]
- RU 2275407 [0009]
- RU 2169166 [0011]
- RU 2401295 [0013]

**Non-patent literature cited in the description**

- **RAGULINA R. I. ; YEMLIN B. N.** *Elektrotermiya Kremniya i Silumina (Electrothermy of Silicon and Silumin)*, 1972, 240 [0002]