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Nanochemical Processes In Solid-Phase Reduction Of Ferrioxide-Silicate Materials

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Solid-phase carbon reduction of ferrioxide-silicate materials have been investigated on example of sedimentary iron ores of Kerch deposit. It was shown that nanochemical iron oxide reduction to sponge iron with flux-mineralizers is accomplished due to ferric carbide and nanocarbon mostly, which are being formed out of initial carbon powdered material by carbide mechanism.

Obtained results caused development of iron ore direct reduction method which is much better of SL/RN method used in industry.

Keywords: Ferrioxide-silicate materials, Nanocarbon, Mineralizers, Nanochemical reduction, Sponge iron.

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1. INTRODUCTION

The problem of iron and steel production enhancement from iron ores production technology was and still remains as actual globally due to permanent need in high-quality and relatively low-price steel and iron semifinished and finished products at different branches of industry. Extensive scientific and scientific-technical investigations in this sphere have led to development (till the end of 20th century) of various cost-effective technologies of ferrioxide materials direct reduction with gaseous hydrogen and single-oxide carbon obtained from natural gas [1]. However, availability of such technologies is being constantly decreased due to increasing costs for natural gas, while interest in methods of solid state reduction of ferrioxide materials with carbon and their scientific substantiation using achievements in nanoscience and nanotechnology is constantly growing [2-4]. Thus, current investigation is devoted to development of conceptions of such processes.

2. EXPERIMENTALS

Sediment ferrioxide-silicate ores with manganese additive from Kerch deposit are used at experimental part of the work. Their solid state reduction at 1000- 1200°C with carbon powdered material, with and without mineralizers presence has been investigated using roentgen-phase, thermogravimetric, electronmicroscopic and chemical methods.

3. RESULTS CONSIDERATON

Radiographs (Fig. 1) of cakes, obtained from mixture of ore and carbon, have verified availability of metal iron and magnetite in them. Wustite and magnetite are available in cake, obtained at 1000 ºС, while in cake, obtained at 1050ºС, their amount is considerably lower, and the main component of cake, obtained at 1200°С is a metal iron. Quantity of the last is 1.5-2 times higher in

case of application of mineralizers, and a phase of nsutite $[MnO(OH)]$ forms. Amount of ferrous silicate $Fe₂SiO₄$ (fayalite) in cake obtained at 1000ºС and 1050ºС-1200ºС remains constant. It shows that its amount depends on quantity of highdispersed silica in charge mixture which reacts generating highdispersed and nanodispersed fayalite under the following scheme:

$$
2FeO + SiO2 \rightarrow Fe2SiO4
$$
 (1)

According to obtained thermogravimetric analysis data (Fig.2) the processes of iron ore reduction with carbon begin at temperature above 450ºС generating magnetite, which partly reduced to wustite at temperature above 1000ºС. The latter coexists with magnetite and metallic iron up to 1050ºС (Fig.1). At higher temperatures (1150-1215°C) sponge iron with fayalite $Fe₂SiO₄$ admixture covered with nanocarbon particles is present.

Experiments with addition of salts-mineralizers show that along with traditional direct iron reduction chemical processes proceeding with the basic reactions:

$$
3Fe2O3 + C \rightarrow 2Fe3O4 + CO
$$
 (2)

$$
\text{Fe}_3\text{O}_4 + \text{C} \rightarrow 3\text{FeO} + \text{CO} \tag{3}
$$

$$
\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO} \tag{4}
$$

intermediate reaction of unstable highdispersed cementite formation is proceeding actively:

$$
3Fe + C \rightarrow Fe_3C \tag{5}
$$

dissociating into sponge iron and nanocarbon particles easily.

Formed cementite is actively interacting with the ironoxide materials at specially selected conditions (optimal ratio of charge components, their dispersion, availability of mineralizers) due to the availability of nanocarbon in its structure and due to the high dispersion of cementite itself under the following schemes:

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Fig. 1 – X-ray diffractogram of Kerch deposit ore (a) and products of its reducing firing at 1000°С (b) and at 1200 °С (c) mixed with carbon powder in 4:1 ratio

Fig. 2 – Thermograms of Kerch deposit ore (a) and its mixture with carbon powder in 4:1 ratio (b)

Fig. 3 – Electronmicroscopic image of nanocarbon (a) and carbonized silicate (b) extracted from sponge iron obtained at 1215°С

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$$
\text{Fe}_2\text{O}_3 + 3\text{C}_{\text{nano}} \rightarrow 2\text{Fe} + 3\text{CO} \tag{6}
$$

$$
Fe2O3 + 3Fe3C \rightarrow 8Fe + 3CO
$$
 (7)

$$
Fe3O4 + 4Fe3C \rightarrow 15Fe + 4CO
$$
 (8)

$$
\text{FeO} + \text{Fe}_3\text{C} \rightarrow 4\text{Fe} + \text{CO} \tag{9}
$$

The process is accompanied with partial dissolution of solid sponge iron microparticles in cementite melt formed at 1160-1180°С, which provides for further liquid metal microdroplets formation. Those microdroplets are purified from adhesively bound silicate inclusions under the influence of flux-mineralizers regulating the surface tension and droplet size as well as their reactivity. After consumption of excess carbon in those droplets for active recovery processes, they are being hardened, transformed mainly again into sponge iron of higher purity, than the original one. This can be represented by following scheme:

Fe₂O₃ + C
$$
\frac{700-1000^\circ C}{2}
$$
 >2FeO + CO; FeO + C $\frac{700-1200^\circ C}{2}$ >Fe + CO; 3nFe + C_nH_m $\frac{700-1000^\circ C}{2}$ >nFe₃C \rightleftharpoons Fe + C
\n
$$
Fe_2O_3 + SiO_2 + C_nH_m + C \longrightarrow 2FeO + SiO_2 + nC + CO + \frac{m}{2}H_2 \longrightarrow \boxed{Fe_2SiO_4 + nC} + CO + \frac{m}{2}H_2
$$
\n(10)

The method of direct sponge iron and cast iron materials reduction from ironoxidesilica materials has been developed and patented based on results obtained. This method is 1.5-2 times exceeding the SL/RN method [1] used now in the industry at its economic efficiency.

4. CONCLUSIONS

Thus, colloid-chemical foundations of direct solid iron oxide materials reduction have been considered, and the determining role of nanoscience achievements and nanotechnological colloidal elements in these processes has been shown.

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