Peculiarities of carbothermic reduction of titanomagnetite ore pellets

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Abstract
The aim of this research was to study the peculiarities of structural transformations of the mineral particles in the process of carbothermic reduction of titanomagnetite ore pellets with a high mass fraction of titanium (20 % TiO_2) within the temperature range of 800-1500 °C, and also to establish technological parameters of this process.
Keywords: TITANOMAGNETITE CONCENTRATE, POLISHED SECTIONS, EDGE, CARBOTHERMIC REDUCTION, SOLID PHASE CHANGES, METALLIC IRON, TITANIUM SLAG

Ukraine possesses large reserves of complex titanium magnetite ores, which use is possible after development of new-type technology for processing of titaniferous concentrates with high content of titanium. The technology ITmk3 (Ironmaking Technology Mark Three) based on process of solidphase reduction of ferriferous pellets in rotary furnaces [1-3] is perspective for processing of high grade (> 8 % TiO_2) titanium magnetite concentrates. The technology ITmk3 is characterized by high rates of quality of the final product, law level of pollutant emissions and rather small specific capital expenditure [4-6].

Research problem statement

Previous researches of carbothermic process of titanium magnetite concentrates reduction with mass fraction of Fe_{tot} 56.5-64.5% and titanium dioxide 3.0-16.7% have shown that in case of metallization, obtaining metal ferriferous product and slag with mass fraction of TiO_2 15.4-62.5% is possible [5]. For development of technology and parameters of technological process it is necessary to study laws of textural-structural and mineralogical transformation in titanium magnetite agglomerate (pellets, briquettes).

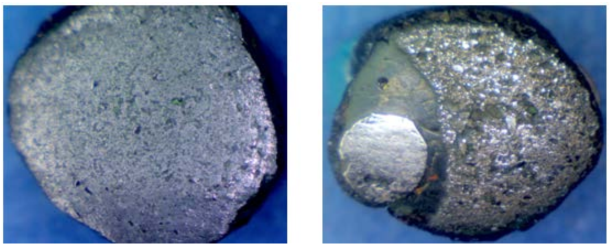
Materials and techniques of research

The object of research was pellets from titanium magnetite concentrate of apatite-ilmenite-titanium magnetite ores [7] with the following composition, mass %: 45.5 FeO; 23.0 Fe_2O_3; 22.03 TiO_2; 1.5 SiO_2; 1.2 Al_2O_3; 0.26 CaO; 3.4 MgO; 0.42 MnO; 0.516 V_2O_5; 0.04 Cr_2O_3. Taking into account recommendations [1, 2], the mass fraction of carbon and fluxing agent in furnace charge of the researched pellets with diameter of 5-10 mm was 20 and 2% respectively.

Results of researches and their discussion

Studies of textural-structural and mineralogical transformations were carried out by methods of macro- and microscopic researches.

The **macroscopic** studies of pellets polished sections have shown that pellets keep uniform structure at the initial stages of reduction (800-900 ºC). At a temperature of 1000 ºC, the coats of sponge metal of 1-1.5 mm in thickness and more emerge at the surface of pellets. At that, the core of pellets remains uniform. With increase of temperature more than 1100 ºC and holding time in cores of pellets, the spotty texture takes place. It is caused by redistribution of metal iron (Fe^o), which is accumulated in the separate microvolumes and forms light bright spots on the darker opaque background of slag zones (Figure 1a), in volume of a pellet. With growth of reduction temperature and increase in soaking time, metal iron concentrates in the form of spherical shapes from 1 to 4-5 mm in size (Figure 1b). At reduction tempe- ratures more than 1250 ºC (soaking of 20-40 min), deformation of spherical shape of pellets is observed that specifies their emolliating. Total loss of the shape takes place only at a temperature more than 1300 ºC and the soaking of 80 minutes.



a) b)

Figure 1. A texture of pellets in case of different parameters of reduction, incr. **5^x**: a) reduction temperature - 1100 ºC, soaking - 20 min.; b) reduction temperature - 1300 ºC, soaking - 40 min. Bright – metal, opaque – slag

Microscopic researches of the pellets reduced at a temperature of 800 °C have shown that there are no significant phase conversions in pellets. At a temperature of 900 °C and soaking of 20-40 min, metal iron (Fe^o) in the form of discharge, which is less than 1-2 microns (Figure 2a), is formed in titanomagnetite.

At reduction temperatures of 1000-1100 ºC, the coat (outer zone) with thickness 1-3 mm and core with diameter of 5-8 mm which size does not depend on temperature and time of reduction emerge in a texture of pellets. Intensive solid-phase changes take place only in ore grains which are less than 40 microns. Fe° in the form of discharge, which is less than 1 micron in size, appears and also the separate microvolumes up to 80 microns in size containing slag are formed. Ore grains less than 20 microns in size are completely changed with formation of border discharge of Fe°. In case of increase in time of reduction up to 40 minutes in the course of reduction of pellets, the similar solid-phase conversions affecting large (up to 0.8 mm) ore grains (Figure 2b) occur.

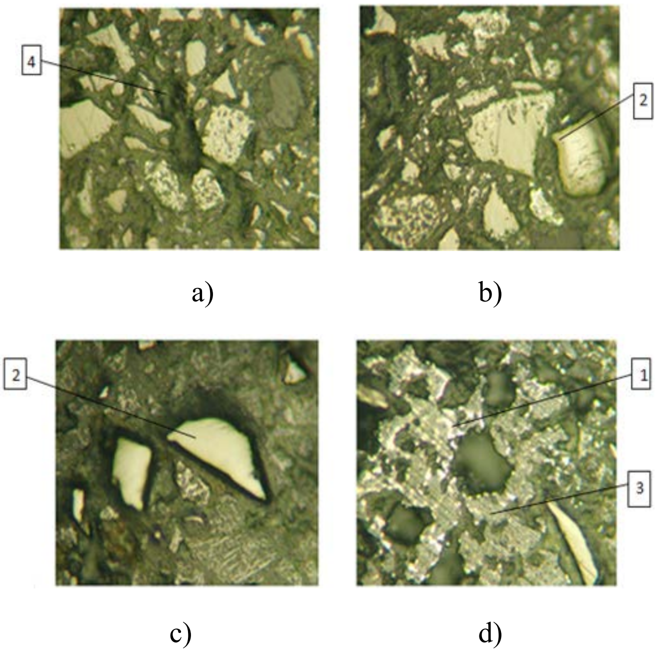


Figure 2. The structural-morphological characteristic of pellets reduced at a temperature of 900 °C (a), 1000 °C (b) and 1100 °C (c, d)

The reflected light without analyzer. Incr. 175ˣ:

a) separation of metal iron in grains of titanomagnetite;

b) solid-phase conversions of grains of titanomagnetite and separation of metal iron in these grains;

c) lattice residual discharge of ilmenite denoting the structure of decay of solid solution;

d) two-phase composition of slag, isolation of Fe °.

1 – metal iron (white); 2 – titanomagnetite (light-cream); 3 – changed sections of titanium magnetite grains (dark-cream); 4 – pores (black).

In the pellets reduced at a temperature of 1100 °C and soaking of 40 min, removing of Fe° from grains of titanomagnetite takes place (Figure 2c). The amount of the slag acquiring two-phase composition increases with increase of reduction duration. Noticeable isolation of Fe° is observed (Figure 2d).

Increase in reduction temperature up to 1200-1250 °C does not provide significant changes of their composition and textural-structural characteristics.

The soaking of pellets at a temperature of 1300 °C leads to essential changes of grains of a concentrate and again formed phases. After soaking of 20-40 min, the grains size of Fe° increases up to 0.1-0.2 mm (Figure 3a, b).

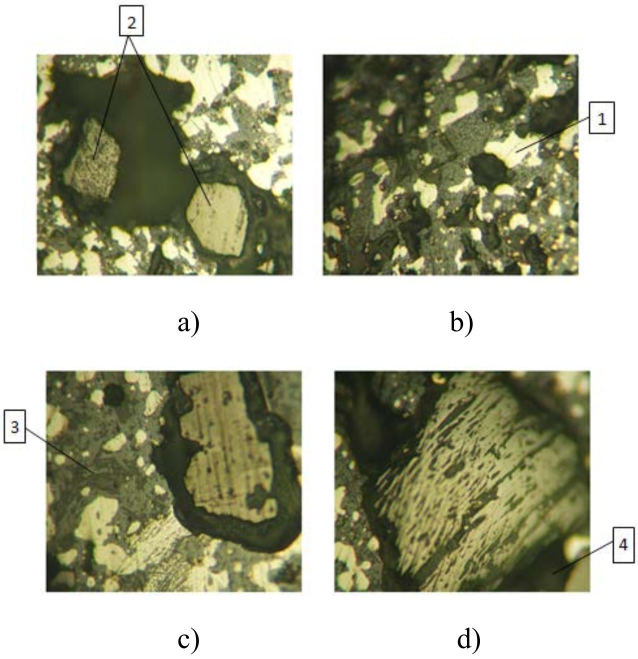


Figure 3. Change of structure and composition of pellets of titanomagnetite reduced at a temperature of 1300 °C and soaking of 40 (a, b) and 50 (c, d) minutes

The reflected light without analyzer. Incr. 200ˣ:

a) two grains of titanomagnetite (soaking of 40 min);

b) coarse ingrained Fe° grains, two-phase slag (soaking of 40 min);

c) block structure of ore grain, coarsening of two-phase slag (soaking of 50 min);

d) grain of titanomagnetite in a solid phase (the rutile-like form of individuals in the aggregate) (soaking of 40 min).

1 – separation of metal iron (white); 2 – changed grains of titanomagnetite to a variable degree (cream of different shades to gray); 3 – slag phases (gray and dark-gray); 4 – pores (black).

Pellets still contain grains of titanomagnetite of 0.1-0.3 mm in size (Figure 3d). In pellets the slag consisting of two phases (Figure 3c, d) is formed and small-sized inclusions of Fe ° of 2-4 microns in size.

In case of long-time soaking of 50-80 min, particles of Fe° coarsen to the size of 1-2 mm (Figure 3a, b, c), some particles integrates into spherical particles with diameter up to 3-5 mm, and in structure of pellets they are distributed in the form of separate sections (fields), (Figure 4c, d).

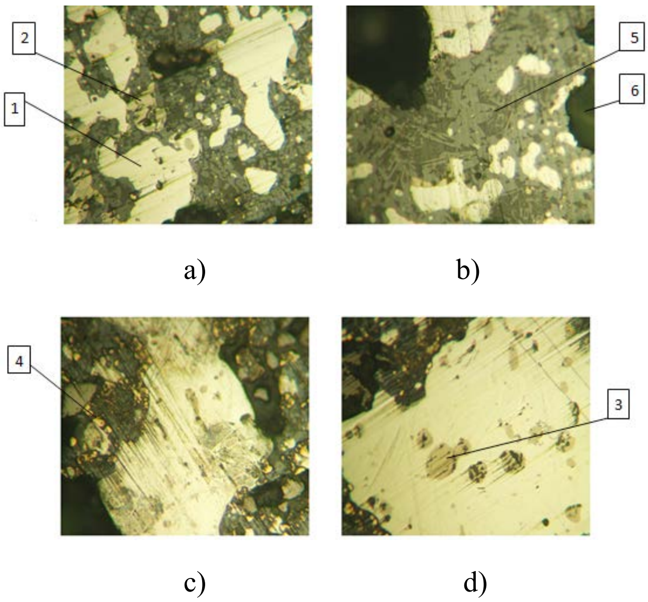


Figure 4. Change of structure and composition of pellets of titanomagnetite reduced at a temperature of 1300 ºC and soaking of 50 (a, b) and 80 (c, d) minutes

The reflected light without analyzer. Incr. 200ˣ:

a) coarse discharge of Feº and phases in slag; emergence of reddish-brown metal, (soaking of 50 min);

b) rutile-like shape of crystals in slag, Feº particles (soaking of 50 min);

c) separation "dirty" (with inclusions at the microlevel) metal in the white, development of "orange" grains in slag (soaking of 80 min);

d) inclusions by the increased content of titanium in Feº (soaking of 80 min).

1 – separation of metal iron (white), 2 – residual ore grains (gray and cream); 3 – separation of metal (reddish-brown); 4 – "orange" grains (orange); 5 – slag phases (gray and dark-gray); 6 – pores (black).

In some particles of Feº round inclusions of reddish-brown color with the increased content of titanium from 8 to 20% (Figure 4d) is observed. In case of soaking of 50 min, slag well crystalized and also consists of two phases (Figure 4a); in case of soaking of 80 min, slag is presented by well-structured crystals of rutile-like form (Figure 4b).

It is also should be noticed that with increase in temperature up to 1300 ºC and hold time to 80 min in reduced pellets, "orange grains" (less than 50 microns) are formed. Their distinctive feature is considerable content of iron (21-50%), titanium (14-45%), manganese (1,24-7,73%) and vanadium (1,4-2,4%).

Reduction of pellets within 5-10 minutes at a temperature of 1500 ºC leads to formation of titanic slag and particles of Feº in the form of reguluses from 5 to 35 mm in size (Figure 5) [8].

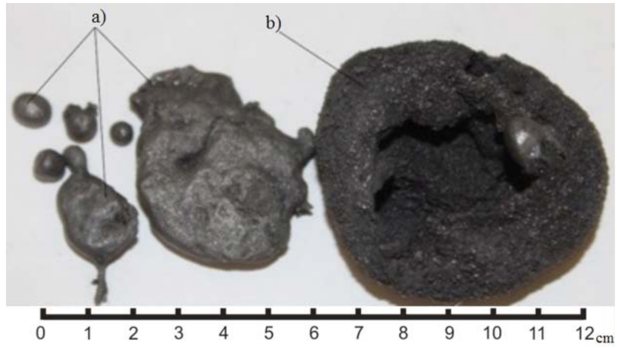


Figure 5. Pellets after reduction in case of 1500 ºC within 5 minutes: a) reguluses of metal; b) titanic slag

The batch of the pellets reduced at a temperature of 1500 ºC within 5-10 min after cooling underwent crushing. The crushed product was divided into magnetic and non-magnetic fractions in magnetic separator with magnetic field 180 mt. The X-ray fluorescent analysis of products of magnetic subdivision by instrument "EXPERT 3L" have shown that as a result of process of carbothermic reduction of titanium magnetite pellets with high mass fraction of titanium (more than 20% of TiO_2) after their crushing and division in magnetic field, obtaining the following products is possible: ferriferous with mass fraction of Feº 93-95% and titaniferous with mass fraction of TiO_2 at least 54%. The titaniferous product can be directed to processing for obtaining pigmental dioxide (TiO_2) or titanium sponge, and ferriferous to smelting of steel in electric furnaces.

Conclusions

The study of features of structural conversions in titanium magnetite pellets in case of carbothermic reduction have shown a basic possibility of application of ITmk3 technology for subdivision of iron and titanium from titanium magnetite grains in Feº in the form of reguluses and titaniferous slag. Implementation of this process requires certain temperature, temporal physical and chemical conditions in the rotary hearth furnace:

- fineness of concentrate should be at least 96-99% of class minus 50 microns;
- the maximum temperature of reduction process should be close to ilmenite melting temperature (1440-1470 °C) and with short term occupancy of titanium magnetite pellets in this temperature zone;
- the technology of restoration should include two stages: heating and preliminary soaking of titanium magnetite pellets at a temperature of 1300 °C within at least 20 min and their subsequent soaking at a temperature about 1500 °C within 5-10 min;
- reduced pellets after cooling undergo crushing and subdivision into magnetic ferriferous fraction with

mass fraction of iron of 93-95% and non-magnetic titaniferous fraction with mass fraction of TiO_2 at least 54% in a magnetic separator.

References

1. Gubin G. V., Piven' V. O. *Suchasni promyslovi sposoby bez koksovoi metalurgii zaliza.* [Modern industrial methods without coke iron metallurgy]. Kryvyi Rih, 2010. 336 p.
2. Razaz Yunes, Opryshko I. A., Loboda P. I. (2011) The analysis of technologies of direct reduction of metal oxides using furnaces with rotating bottom. *Bulletin of the National Technical University of Ukraine "Kyiv Polytechnic Institute". Mechanical Engineering Series.* No 61, p.p. 184-192.
3. Isao Kobayashi, Kobe Steel, «Development of ITmk3 Process and Iron Ore», *Conference of ITmk3 family*, April 3, 2009, Kyiv.
4. Kopot' N. N., Rybkin V. S., Evstyugin S. N., Gorbachev V. A., Leont'yev L. I. (2008) Ways of lowering of iron prime cost of direct reduction. *Stal'*. No 1, p.p. 4-5.
5. Sadykhov G. B., Karyazin I. A. (2007) Research titanovanadium slags of process of direct obtaining of iron from titanium magnetite concentrates. *Metally*. No 6, p.p. 3-12.
6. Tkach V. V., Gubin G. V., Orel T. V. (2005) The modern technology of obtaining marketable products of high added value under conditions of mining and processing works. *Razrabotka rudnykh mestorozhdeniy*. No 88, p.p. 88-92.
7. Zima S. N. (2007) Mineralog-petrographic features of apatite-ilmenite-titanium magnetite ore of Krapivinskoye field. *Novoe v tekhnologii, tekhnike i pererabotke mineral'nogo syr'ya*. Kryvyi Rih, 2007, p.p. 40-52.
8. Baboshko D. Yu., Tkach V. V., Ermak L. V., Orel T. V. (2014) Carbothermic reduction of titanium magnetite concentrate with the high content of titanium. *Metallurgicheskaya i gornorudnaya promyshlennost'*. No 4, p.p. 3-5.