Researching of physicochemical and structural-phase transformations in carbothermal titanomagnetite concentrates reduction for sustainable development of raw materials base of metallurgical enterprises

Dmytro Baboshko1, Lev Saithareiev2, Hennadiy Hubin2, Oksana Vodennikova3, and Ihor Skidin1

1Kryvyi Rih National University, Ferrous metals metallurgy & foundry Department, Kryvyi Rih, Ukraine
2Kryvyi Rih National University, Occupational safety & civil security Department, Kryvyi Rih, Ukraine
3Zaporizhzhia National University, Metallurgy Department, Zaporizhzhia, Ukraine

Abstract. This study displays results of carbothermal reduction researches of titanomagnetite concentrate obtained during complex apatite-titanomagnetite-ilmenite ore dressing. The mineral composition was analyzed and the structural and textural features of the titaniferous ore of Kropivensky deposit and the titanomagnetite concentrate obtained from it were revealed. The mechanism of solid-phase carbothermal titanomagnetite concentrate reduction is investigated. Temperature-time parameters have been discovered to ensure the formation of both products with the maximum yields of iron and titanium from metal and slag-phase during titanomagnetite concentrate reduction. One-stage resource-saving flow chart of titanomagnetite concentrate processing with mass fraction up to 25% TiO2 is developed. It allows to obtain two marketable products: granular cast iron (92-96.5% Fe, 3.4-3.7% C, 0.5% V) in 57% yield and titaniferous slag (50-55% TiO2, up to 7.4% FeO) in 43% yield.

Introduction

Within the framework of the stable metallurgy development program, the team of the Ferrous metals metallurgy and foundry Department of Kryvyi Rih National University scientists deals with the following important tasks: improving the hot-rolled steel plate technology [1] and determining the optimal parameters for the electrical treatment of foundry steels during casting [2]. Another area of research is the development of recommendations for the complex titanium ores involvement in processing. [3]

The rapid development of the metallurgical complex has led to a reducing of quality iron ore reserves amount. In the near future, they will be replaced by complex ores that can meet the needs of ferrous and non-ferrous metallurgy companies. Ukraine has significant complex ore of apatite-titanomagnetite-ilmenite composition reserves. The technologies of their preparation for metallurgical conversion make it possible to obtain basic ilmenite and apatite commodity concentrates and, in addition, titanomagnetite, which can contain 46-52% of Fe and 20-25% of TiO2.

Titanomagnetite concentrate is not currently processed by existing metallurgical enterprises in Ukraine, but it is a promising raw material for the sustainable development of cast iron, steel, titania (TiO2) and metallic titanium. The development and implementation of processing technology for this concentrate will allow the storage of valuable mineral components in the waste heaps. Extant technologies include the use of two-stage processing, which consists of pre-reduction and ore-thermal electric melting, followed by separation into industrial products. These technologies are characterized by high energy consumption and environmental hazards. Therefore, research with the discovering and justification of technical and technological solutions for the processing of titanomagnetite concentrates with a high content of TiO2 goal is relevant and important for the sustained development of metallurgy.

In research works [4-7], a number of experiments were conducted on solid-phase reduction of titanomagnetite concentrates with mass fraction of Fe 56.5-64.5% and up to 16.7% TiO2. It has been shown that slag with a wide range of chemical composition from 15.4 to 62.5% of TiO2 were obtained after their reduction. This is an important basis for studying the iron-containing and titaniferous phases formation mechanism, as well as the allocation of Fe and Ti between them. The analysis of those studies’ results does not allow us to completely determine the peculiarities of the structural-phase titanomagnetite transformations at different temperature-time parameters of the carbothermal reduction process. In addition, the titanomagnetite concentrates reduction process with a TiO2 mass fraction of 20-25% has not been studied.
For carbothermic reduction process, a titanomagnetite concentrate obtained after the apatite-
titanomagnetite-ilmenite ore dressing of the Kropivensky
deposit was used, having the following composition,
mass fraction:%: 45.5 FeO; 23.0 Fe₂O₃; 22.03 TiO₂; 1.5
SiO₂; 1.2 Al₂O₃; 0.26 CaO; 3.4 MgO; 0.42 MnO; 0.516
V₂O₅; 0.04 Cr₂O₃ [8, 9].

Researched ore is low-concentrated, sometimes
contain schlier with 1-2 m capacity of high-concentrated
varieties. The total content of ore minerals does not
exceed 10%. The ore has an apatite-titanomagnetite-
ilmenite composition with variations in the ratio of
titanomagnetite / ilmenite from 1/1 to 1/5. The amount of
apatite is 1-3%. The ores of the deposit are characterized
by a Fe/TiO₂ ratio from 1.5 to 4.0.

A defining characteristic of the magmatic process
that has led to the titanium ores formation is the fact that
minerals are being formed under conditions of constant
change in the chemical composition of the residual melt
and the individual components in it. In addition,
differentiation (separation) of the melt and the arrival of
new magma portions can occur. This creates even more
complicated crystallization conditions, which are
accompanied by the melting of previously formed
minerals grains and even their complete melting and
digestion. Lowering the temperature in the magmatic cell
can lead to the separation of mineral phases already at
the solid solution stage, such as ilmenite, as well as Mg–
Al and Ti – spinels in magnetite. Sometimes magnetite in
pyroxene and others. The peculiarity of all structures of
the solid solution decomposition is a very small sized
inclusions of one mineral in another (1-2 μm), which
in the future, in the industrial ores processing leads to
different technological difficulties.

Titanomagnetite is the predominant ore mineral in
the ore deposit, in some samples its mass fraction can be
up to 13.5% [10,11].

The following research methods were used:
microscopy, spectral, structural-textural and X-ray
fluorescence analysis.

For roasting and sintering concentrate by method ore
coarsening charge, following materials were used:
combined bentonite and FERROFORM polymer, flux
additive CaF₂, and reductant graphite with minimal
mineral content.

**Results and discussions**

In the study of polished sections under the microscope
the titanomagnetite unusualness is noticeable, it is more
similar to ilmenite in optical characteristics. If these
minerals are separated, in the form of isolated grains, it
is difficult to distinguish them. They are easier to
distinguish in joint inclusions – by a noticeable reddish
tint in the color of titanomagnetite (Fig. 1, a, b). In
addition, ilmenite appears to be lighter, which is most
likely due to the Fe₂O₃ impurity in its composition.

In some grains of titanomagnetite under the
microscope, the lamellar ilmenite inclusions in the form
of decomposition structures of a solid solution are easy
to identify (Fig. 1, c, d). The partial oxidation and
leaching of the magnetite component of titanomagnetite
under the weathering bark on gabbro-peridotites impact
seems to present a true picture of the titanomagnetite
grains structure and composition. The study of such ore
samples using a microscope made it possible to
categorize the titanomagnetite under study, to
understand its nature and to develop technologies for the
mechanical ore dressing and the subsequent heat
treatment of titanomagnetite concentrate.

**Fig. 1.** The ilmenite and titanomagnetite ratio in joint inclusions:
a) morphology of titanomagnetite and ilmenite grains;
b) idiomorphism of ilmenite, apatite and sulfide compared to
later titanomagnetite; c) lamellar inclusions of ilmenite in
titanomagnetite; d) homogeneous titanomagnetite (lower part
of the grain), which fades into decay structures with ilmenite
plates (upper part of the grain). 1 – titanomagnetite (creamy
with a reddish tint), 2 – ilmenite (white with a grayish tint),
3 – iron sulfides (white), 4 – apatite and silicates (different shades
of gray).

Microscopy revealed that the grains of
titanomagnetite, separated in space, have almost the
same size (from 0.03 mm to 0.6 mm) as ilmenite, and are
often with it in the fusion (Fig. 2, a, b, c) [12].

Single grains have a homogeneous (homogeneous)
structure. Most often they are an aggregate of two or
more mineral phases. They coalesce at a very thin
submicron level, being elements of solid solution
decomposition structures. Therefore, the term
“titanomagnetite” is a fairly conditional term. Separate
grains (and essentially aggregates of two or four mineral
phases), whose chemical composition is determined by
the FeO, TiO₂ and Fe₂O₃ content, are the titanomagnetites
of this deposit. They have high magnetic characteristics.
These grains are characterized by the different mineral
phases’ presence: magnetite, ilmenite, and Al-Mg spinel
in small quantities, which are formed after the collapse
of the solid mortar. The ratio of these phases in
titanomagnetite grains is different.

The magnetite forms the basis of the grain matrix
into which the lamellar ilmenite or ulvospinel excretions
are immersed and the micro-grain “relict-ilmenite”
(Fig. 2). The lamellar isolates of ulvospinel generally have a thickness of up to 2-3 microns. Single titanomagnetite grains have lamellar isolates of ilmenite or ulvospinel up to 8-10 microns in size. At the same time there are grains of titanomagnetite with different saturation structure and size of secretions (plates) of ilmenite or ulvospinel (Fig. 1, c, d and 2, a, b). The orientation of the plates according to the octahedral separation in magnetite is characteristic of titanomagnetite, often with the formation of lattice structures (Fig. 2, a).

The micrograin “relict – ilmenite” is often semi-alloyed, sometimes they are solitary, but more often concentrated in groups (Fig. 2, b, c, d). The size of micro-grains inclusions is 0.05 – 0.1 mm. These are micro inclusions its remains “Magnetite” magma beneficiated by titanium. The presence of “relict – ilmenite” micro grain causes a high (up to 25%) content of TiO₂ in titanomagnetite grains [13].

Titanomagnetite is also characterized by the presence of a higher concentration of V than in ilmenite. This is due to the fact that Fe has a close crystal-chemical bond with V, and since ilmenite has a smaller proportion of Fe, the concentration of V in it will be lower.

Based on the study of the morphological structures of apatite-titanomagnetite-ilmenite ore, the classification of titanomagnetite grains is made: - grains with fine ilmenite in the magnetite matrix (Fe – 34.25 ± 1.4%, Ti – 11.37 ± 0.37%); - grains having the structure of equally distributed lamellar secretions of ilmenite in the magnetite matrix (Fe – 31.24 ± 1.73%, Ti – 18.65 ± 1.08%);

Analysis of these types of titanomagnetite concentrate grains confirmed their complex structure and showed that the reduction conditions of this concentrate will be significantly different from the reduction parameters of iron-containing magnetite concentrate.

The calculations show that the magnetite matrix of titanomagnetite grain contains up to 34.6% of Fe, and in the ilmenite particle – up to 15% of Fe. The different structure of the grains and their elemental composition make it necessary to determine the optimal temperature and time parameters for the reduction of the magnetite matrix and the release of ilmenite, which will achieve the maximum extraction of Fe and TiO₂ in the industrial products.

It is established that the obtained coils have satisfactory characteristics for their further reduction: porosity – 30-35%, compressive strength – 1.32 kg/pellet (for dry – 2.7 kg/pellet), reset strength – 4.2 times.

The process of carbothermal reduction of coils with a diameter of 10-14 mm was carried out in the temperature range of 800-1500 °C.

Based on the studies of the morphological structures of ulvospinel, ilmenite ore, the classification of titanomagnetite grains is made: - grains with fine ilmenite in the magnetite matrix (Fe – 42.36 ± 2.18%, Ti – 14.47 ± 0.96%); - grains having the structure of uniformly distributed lamellar secretions of ilmenite in the magnetite matrix (Fe – 34.25 ± 1.4%, Ti – 11.37 ± 0.37%); - grains having the structure of equally distributed lamellar secretions of ilmenite and separate microgranules of “relict-ilmenite” in the magnetite matrix (Fe – 31.24 ± 1.73%, Ti – 18.65 ± 1.08%).

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Studies of the pellet’s microstructure at different temperature-time parameters of the treatment process showed that the reduction of the titanomagnetite concentrate happened in two temperature-time periods, in which significant physicochemical and structural-phase transformations occur.

In the first period (“low-temperature zone”, 800-1000 °C) there is a physicochemical transformation of iron-containing silicates (olivine and pyroxene) with the formation of magnetite and its subsequent reduction to Fe⁰. At 900 °C, solid-phase changes start in titanomagnetite grains. Around the grains appears a dark border of 10–15 microns thick, characterized by a higher titanium content (Fig. 3, a).

It happens as a result of the restoration of the magnetite matrix of the grain with the formation of Fe⁰ in the form of droplets less than 0.1 μm and its diffusive removal beyond the grain boundary (Fig. 3, b).

At 1000 °C in volume of pellets solid-phase changes are accelerating. Up to 1 microns of Fe⁰ appear. With increasing the holding time at this temperature up to 40 min, the intensity of both the reduction of the magnetite matrix in titanomagnetite grains up to 0.06 mm and the release of Fe⁰ increases. There is an intense formation of a metal sponge (Fig. 3, c, d). In grains of more than 0.06 mm in size, the concentration of which is not more than 20% in the concentrate, solid-phase transformations with separation of Fe do not occur.

In the second thermo-time period (“high-temperature zone”, 1000–1300 °C), the accumulations of Fe⁰ continue. Titanomagnetite grains complete the reduction of the magnetite grain matrix. At a temperature of 1200 °C, “relict-ilmenite” and a grid of ilmenite remain in place of the titanomagnetite grains, which are inherited from the structures of decomposition of the solid mortar (Fig. 3, c).
Exposure for 5-40 min at 1300 °C ensures the aggregation of Fe\(^{0}\) clusters up to 0.1-0.2 mm, and shutter speed up to 50 min – the appearance of regions of Fe\(^{0}\) spherical in diameter up to 2 mm. The slag titanium phase begins to form from the ilmenite mesh. At the end of 80 min, the enlargement of Fe\(^{0}\) regions to 3.5 mm continues, the content of Ti decreases to 2%, but in them there are significant accumulations and separate inclusions of secretions with the content of Ti up to 31% (Fig. 3, d). The Fe content in the slag phase gradually decreases from 38% to 25%, and the Ti content increases from 23% to 39% (Fig. 3, d) [3].

For maximum extraction of Fe\(^{0}\) and TiO\(_2\) into the iron and titanium phase, a complete reduction of the magnetite particle in all grain types is observed, which is observed as a result of holding for 20 min at 1300 °C (Table 1), as well as further raising of the temperature to 1500 °C with holding 5 min. This ensures the reduction of FeO in the ilmenite particle of the grains. The total degree of metallization of the coils thus increases to 94%.

The reduced product (Fig. 4, a) is a shell-shaped porous formation of a slag phase with a wall thickness of 2-3 mm, and a separated iron phase in the form of spherical particles up to 30 mm (Fig. 4, b). The slag phase is mainly composed of thin-needle and thin-fiber aggregates of rutile and anatase with up to several micrometers thickness (Fig. 4, c).

Sometimes, in the slag phase, glass inclusions and single residual semi-melted titanomagnetite ore grains of 0.04 × 0.07 and 0.07 × 0.15 mm with a FeO border 1-3 μm thick are observed around them.

Fig. 3. Structural transformations in coils reduced at 900-1300 °C: 1 – grains of titanomagnetite (cream color); 2 – allocation of metallic iron (white color); 3 – ilmenite mesh; 4 – slag phase (dark gray and gray).

Fig. 4. Reduced product (a), the microstructure (b, c; x200) and the chemical composition (mass, %) Of the products of reduction: 1 – the separation of metallic iron (white color); 2 – slag titanium phase (different shades of gray); 3 – semi-melted grains of titanomagnetite (cream color).

Thus, the parameters of a two-step process for the reduction of titanomagnetite concentrate were determined, which ensure the formation of iron-containing and titaniferous products with maximum extraction of Fe\(^{0}\) and TiO\(_2\) in them. These parameters are: I degree – reduction of the magnetite particle with increasing temperature from 800 °C to 1300 °C; II degree – restoration of ilmenite particle with increasing temperature from 1300 °C to 1500 °C.

It should be noted that the formation of metal granules from grains of titanomagnetite is a complex process that happens due to the diffusion of Fe\(^{0}\) microparticles into the intergranular space with its subsequent enlargement due to autogenesis. The forces of adsorption attraction, which are caused by covalent, ionic, polarizing or intermolecular (dispersion) forces, have a significant effect. But several types of these forces are possible at the same time. As the temperature of the process increases, the formation of liquid metal clusters into a spherical shape continues due to coalescence (coagulation). In order to prevent impediments to the coagulation processes of the iron particles and the inhibition of the process of separation of the metallic and slag titaniferous phases, this phase must be converted to a visco-plastic state.

Table 1. Chemical composition of slag phase at the temperature reduction of during 800-1300 °C temperatures and holding time of 20 and minutes.

| Holding time | Series of tests | Fe   | Ti   | V    | Si   | Mn   |
|--------------|----------------|------|------|------|------|------|
| 20 min       | 1              | 16.7 | 37.58| 0.58 | 0.42 | 2.42 |
|              | 2              | 14.4 | 32.97| 0.17 | 0.85 | 0.47 |
|              | Average        | 15.65±1.3| 35.28±2.86| 0.38±0.25| 0.64±0.27| 1.45±1.21|
| 40 min       | 1              | 36.61| 29.37| 0.35 | 2.13 | 1.42 |
|              | 2              | 42.13| 30.68| 0.22 | 1.42 | 1.81 |
|              | Average        | 39.37±3.4| 30.03±0.81| 0.29±0.08| 1.78±0.44| 1.62±0.24|
Fig. 5. Chart of structural-phase transformation in the carbothermal reduction of the pelletized titanomagnetite concentrate.

Fig. 6. Flow chart of titanomagnetite concentrate processing.
It is advisable to carry out the process of two-stage reduction with certain technological parameters in a direct reduction furnace with annular hearth, since the final product is not granulated iron, but granular cast iron. This oven has high operational reliability, economy and environment friendliness. Chart of structural-phase transformation at certain parameters. The carbothermal reduction of the titanomagnetite concentrate in this furnace is shown in Fig. 5.

According to the results of the research, the working area of the furnace is divided into technological sections (Fig. 5):

- section I – loading of the material and its heating from 600 °C to a temperature of 800 °C;
- section II – heating from a temperature of 800 °C to 1300 °C with a speed of 20 °C/min and holding for 15-20 min – indirect reduction of the magnetite part of the titanomagnetite grain;
- section III – heating from a temperature of 1300 °C to 1470-1500 °C at a speed of 50 °C/min and holding for 5 min – direct reduction of residual magnetite and FeO from ilmenite parts of titanomagnetite grains.

The flow chart of titanomagnetite concentrate processing for obtaining marketable products with maximum extraction of FeO and TiO2 in them was developed and tested (Fig. 6). This scheme includes the basic production operations: 1 – occlusion of charge materials and their drying, 2 – heating, reduction and melting of coils in a high-temperature unit, 3 – cooling the product, 4 – grinding and dividing of the obtained product into magnetic and non-magnetic fraction.

The yield of the iron-containing fraction was 57% in the form of cast iron granules (92-96.5% Fe; 3.4-3.7% C, 0.5% V), the yield of the slag fraction was 43% in the form of titaniferous slag with 50-55% TiO2 and up to 7.4% FeO.

Conclusions

As a result of the research, it was discovered that the structural-phase transformations during the carbothermal reduction of the pelletized titanomagnetite concentrate proceeds by the following scheme: physicochemical and structural transformations of the olivine and pyroxene minerals at 800 °C; the beginning of the magnetite matrix reduction of grain with the iron diffusion into the intergranular space at 900 °C; complete reduction of the magnetite component of grain with the ilmenite mesh and “relict-ilmenite” formation at 1200 °C; the emergence of the titaniferous phase as a result of the ilmenite grid reducing and the “relict-ilmenite” at 1300-1500 °C. The parameters of the two-step reduction process of titanomagnetite concentrate, which provide the formation of iron-containing and titaniferous products with maximum extraction of FeO and TiO2 in them, are experimentally discovered. I step – magnetite phase reduction with increasing temperature from 800 °C to 1300 °C and holding for 20 min at a final temperature (it provides complete reduction of the magnetite phase of grain). II step – reduction of ilmenite phase with increasing temperature from 1300 °C to 1500 °C with holding at a final temperature of 5 min. A one-stage resource-saving flow chart of titanomagnetite concentrate processing with a mass fraction up to 25% TiO2 has been developed based on carbothermal reduction of pellets in an annular hearth furnace. It allows to obtain two marketable products: granular cast iron (92-96.5% Fe, 3.4-3.7% C, 0.5% V) in 57% yield and titaniferous slag (50-55% TiO2, up to 7.4% FeO) in 43% yield.

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