PIROMETALLURGICAL TREATMENT OF TITANOMAGNETITE ORE FROM THE URAL REGION

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ABSTRACT

Composite ores are more often used for production of iron in connection with reserve depletion of traditional ore crude in the regions with developed metallurgy. In particular, the majority of perspective ferrum-ore deposits of the Urals are presented by titanferous magnetite ores which contain a significant amount of titanium and vanadium alongside with ferrum. Thus, the deposits of titanferous magnetites of the Southern Urals on the average contain about 20 % of Fe, 8,7 % TiO_2 *and 0,24 %* V_2O_5*. Due to a high content of titanium oxides it is impossible or it is inexpedient to process such ores in blast furnaces. During work just on titanferous magnetite ore refractory titanium-containing slags are formed in a blast furnace, and in case of its dilution by ores of different types the titanium due to the small content in slag is thrown out. It is often impossible to separate such ores into ferriferous and titanferous concentrates because ferrum and titanium are present in the same minerals.*

This work attempts to selectively reduce ferrum in solid oxide and to separate metallic iron from titanferous slag with fast fusion. Solid-phase reduction of ferrum has been carried out with carbon at temperature of 1000 ... 1300°C. In products of solid-phase reduction the extremely disperse mix of metal iron and only partially reduced titanium oxides have been achieved. It is impossible to separate such a mix mechanically. However, the fast fusion of the mix allowed separating it into cast iron and slag with the high content of titanium. Thus the cast iron contained less than 0,1 % of titanium, and the slag did not contain practically any ferrum.

1. INTRODUCTION

In connection with exhaustion of stocks of accessible and easily processed ores, it is often necessary to use poor and complex ores for the alloying of metal. Since the extracted metals in such ores, as a rule, are composed of complex oxides and form firm solutions of oxides or thin growths of minerals they can hardly be enriched or cannot be concentrated with traditional methods at all. Such types of ores include titanferous magnetites which are rather widespread and can be a source of ferrum, titanium and vanadium. However, a variation in their chemical and mineral structure demands the use of various methods for their enrichment and separation of metals. It is especially difficult to process ores in which the most valuable elements – ferrum, titanium and vanadium form solid solutions and are present in the same minerals [1-3].

Earlier we established [4-9] that negatively charged anionic (oxygen) vacancies with high mobility are formed in the lattice of oxides during the solid-phase reduction of metals from oxides as a result of withdrawal of oxygen by a reducer. Due to the ionic character of the link in the lattice of oxides the charge of absent oxygen ions should be necessarily compensated by "redundant" electrons, coming from the reducer. These redundant electrons connected with vacancies are localized at cations with the highest affinity to electron. The complex “anionic vacancy – cation of the lowered charge” or “anionic vacancy – atom of metal” is formed as a result. Displacement of vacancies to places of their drain on defects of the oxide crystal structure is accompanied by hauling of atoms of the most easily reduced metals present at the oxide lattice. It creates con-

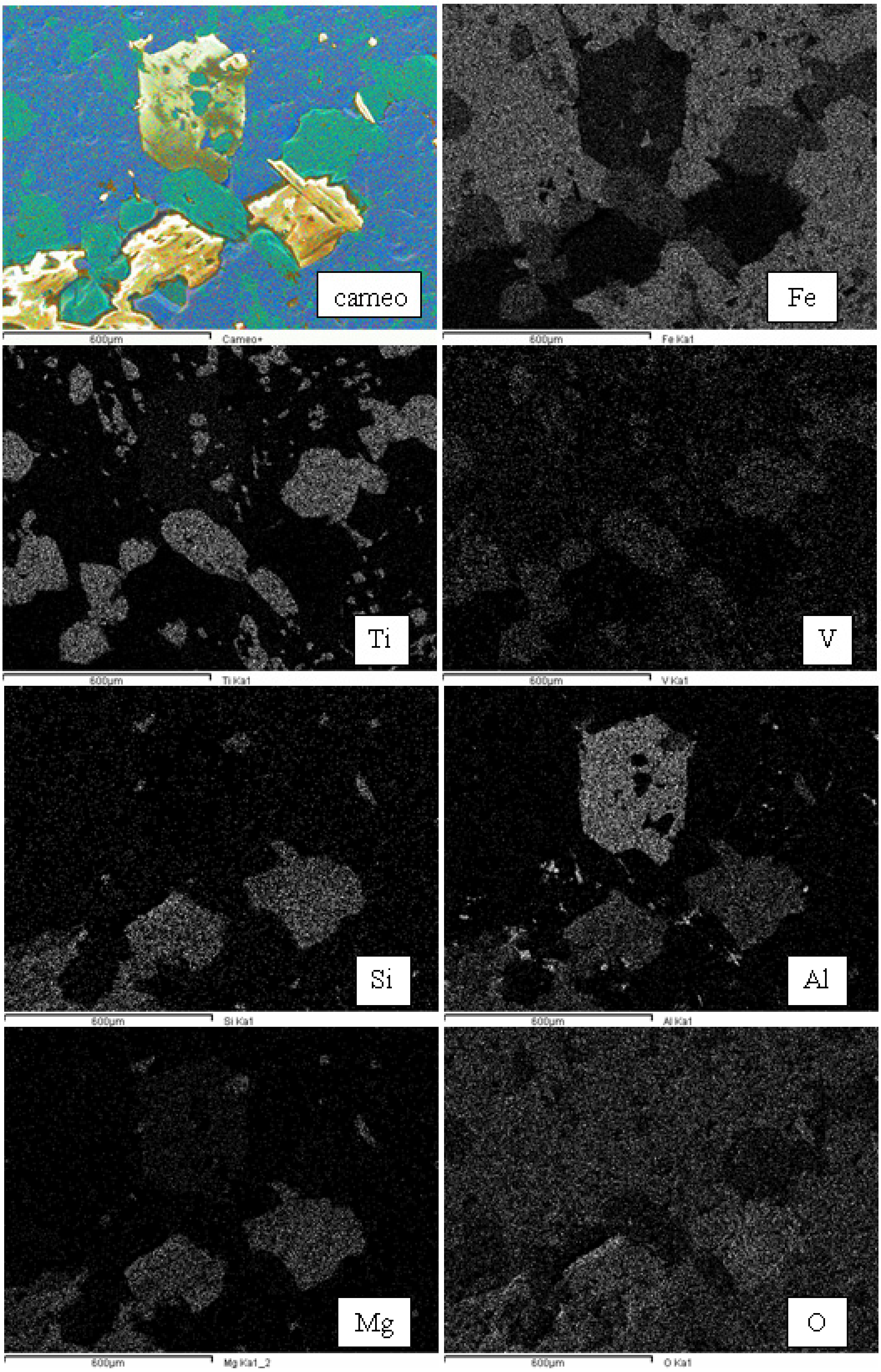

Figure 1: Distribution of elements in ore minerals

ditions for selective reduction of metals from complex oxides and a chance of their subsequent separation from the oxide phases.

Based on these prerequisites, the present work investigates the opportunity of solid-phase concentration and the liquid-phase separation of titanomagnetite components formed by titanium solutions in magnetite and vanadium – in magnetite and ilmenite.

2. MAIN PART

2.1 Subject and Method of Inquiry

A process of selective solid-phase metal reduction from titanomagneties deposits of the Urals Mountains has been investigated; metal reduction by carbon from lump ore and from products of dressing – the ilmenite concentrate.

In the initial condition the lump ore consisted of ore grains and impregnations of the lean material presented by silicates of the serpentine-chlorite group of $Mg_3[Si_2O_5](OH)_4$ – $(Mg,Al,Fe)_3[Si_2O_5](OH)_4$. In the ore part prevailed spinel grains of titanomagnetite (solution of titanium oxides in magnetite Fe_3O_4) and magnetite Fe_3O_4, isolated grains of ilmenite $FeO{\cdot}TiO_2$ were present in a small amount. Uneven and variable content of titanium in titanomagnetite grains has been found (fig. 1).

On the average, the content of elements on the area of the polished section represented on fig. 1 constituted:

Table 1: The chemical compound of titanomagnetite, % at:

Element	Fe	Ti	V	Al	Mg	Si	Mn	Na	Zn	Ca	O
Content	21, 57	4,00	0,31	5,59	4,15	1,76	0,09	0,25	0,09	0,05	62,14

Pieces of ore have been covered with graphite powder and in a graphite crucible they were placed in a resistance furnace with a graphite heater. The furnace was heated to 1100, 1200 or 1300°C, kept for 1, 2, or 3 hours and cooled. The pieces were cut, and on the cut surface polished sections were made which were studied using optical microscopes. A part of the samples were studied on the raster electronic microscope JEOL JSM-6460LV supplied with wave- and energy-dispersive analyzers.

As a result of regenerative heating the samples acquired a zonal structure. The regional zone of all samples had a dense structure. Fissured structure was kept in the internal part of the samples. The nonmetallic substance in the samples has lost water and decrystallized into minerals of the olivine group $(Mg, Fe)_2{\cdot}SiO_4$, cordierite $2MgO{\cdot}Al_2O_3{\cdot}5SiO_2$ and glass. The rough lattice or lineage structure of decomposition formed by excretions of ilmenite in some large titanomagnetite grains was discovered in all samples on all sample sections (fig. 2). Fine titanomagnetie grains in the same samples have kept a homogeneous structure. However inside of a silicate phase surrounding these grains there were ilmenite crystals of the second generation.

The formed structure of decomposition is also characteristic for many natural ores [9,10], therefore it should be classified as a result of thermal decomposition of the supersaturated solid solution of titanium oxides in magnetite. In large grains, the decomposition has led to formation of a new phase (of ilmenite) inside of grains on crystalographic planes that have given a characteristic mesh structure. In fine grains, the redundant component of the solution (titanium) due to the small size and the developed surface of the grains had time to diffuse to their surface where it has been absorbed by the accommodating silicate phase. Upon subsequent cooling it was formed from the silicate solution in the form of fine ilmenite crystals of the new generation.

The zonal structure of ore samples reveals the whole sequence of the crystal-chemical transformations during decomposition and reduction of titanomagnetite. After exudation of moisture and the redundant ilmentie allocation, the reducing of ferrum in the form of separate metal particles contained in a "slag" silicate phase begins (fig.3, a*)*. These new formations (metal and slag) emerge on surfaces of initial titanomagnetite grains,

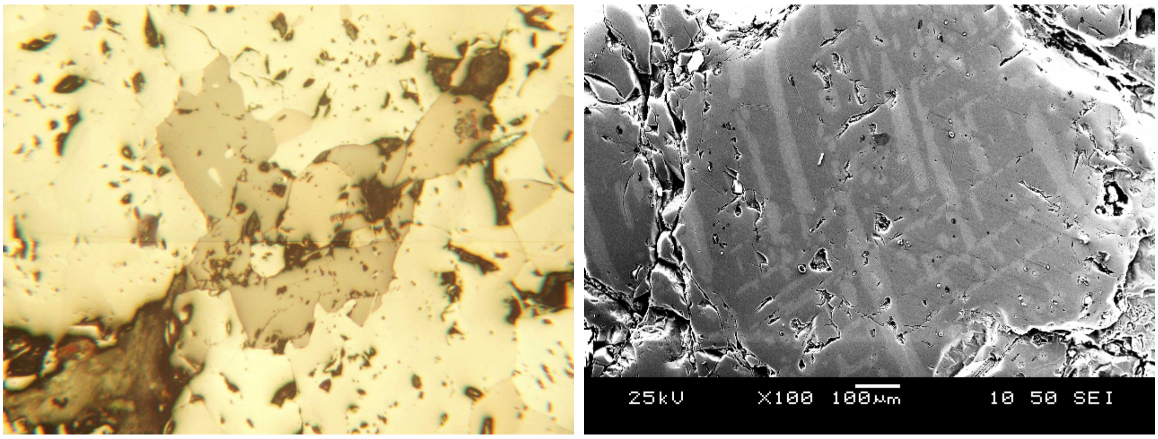

Figure 2: Ilmenite excretions in the original and the regenerative heated ore

and on the borders of crystallographic blocks inside of the initial titanomagnetite grain and also split up the initial grain into smaller blocks. Some of the newly formed blocks reveal a similarity of optical properties with properties of the initial titanomagnetite (spinel), but the majority have a pronounced complex of ilmenite $FeO \cdot TiO_2$ properties.

In future the shell of a new phase is formed on a surface of ilmenite grains generated after excretion of ferrum (fig. 3, *b*). According to results of the petrographic analysis it is defined as ferrum dititanates $FeO \cdot 2TiO_2$. It is interesting to note that this phase comes to light only in the form of the shell, bordering faded out (as if they are "melting") ilmenite grains. The "melting" ilmenite grain leaves behind the branchy metal framework – a metallic sponge the intervals of which are filled with a slag phase (fig. 3, b*)*.

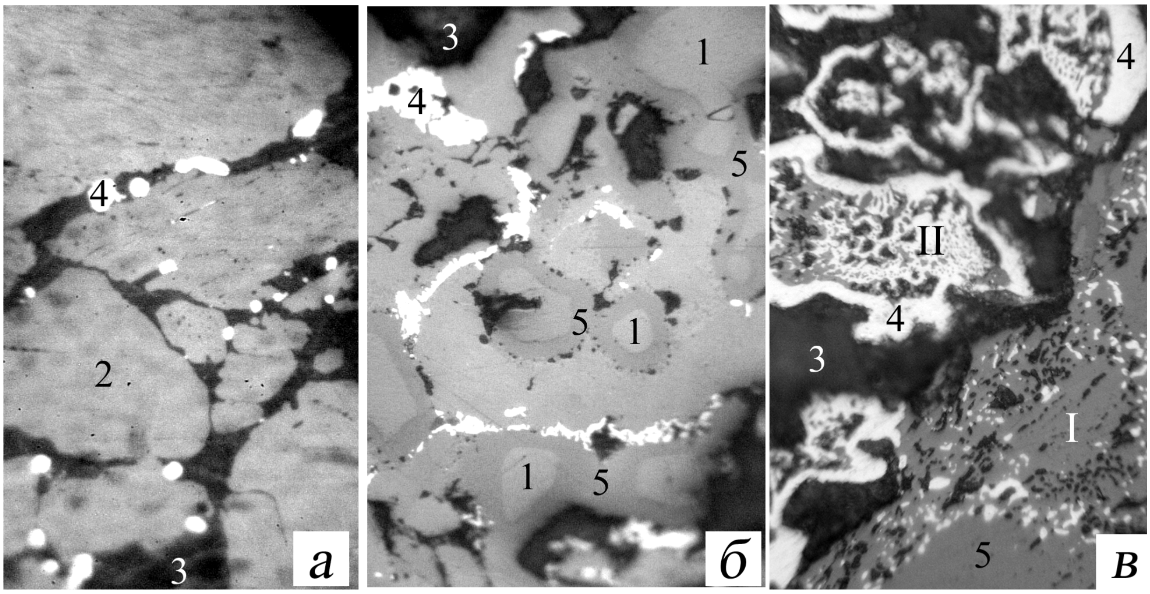

Figure 3: The sequence of titanomagnetite transformation during reduction, x200: a – crushing of titanomagnetite grains with new formations of silicate and metallic phases and their transformation into ilmenite grains, b – formation of the border of ferrum dititanate on ilmenite grains, c – disintegration of ferrum dititanate (I – the initial stage, II – the final stage). 1 – ilmenite, 2 – titanomagnetite, 3 – silicates, 4 – metal, 5 – ferrum dititanate

After the disappearance of ilmenite the remainder of ferrum dititanate breaks down with formation of an even more disperse structure of disintegration consisting of a metal and oxide phase. The latter sharply differs from the other oxides in the optical properties (fig.4). In a transmitted light it is colored in black and is opaque. In the reflected light it has pinkish-purple coloring with the intensive pleochroism of reflection, and the intensity of coloring and intensity of pleochroism change significantly. Based on the optical properties this phase can be confidently referred to anosovite the general formula of which is $m[(Ti,Al,Fe)_2O_3 \cdot TiO_2] \cdot n[(Ti,Mg,Fe)O\ 2TiO_2]$, and the optical properties change with changing of a ratio of quantities Ti^{3+} and Ti^{4+}. With the quantity increase of Ti^{3+} the intensity of coloring and pleochroism increases [11].

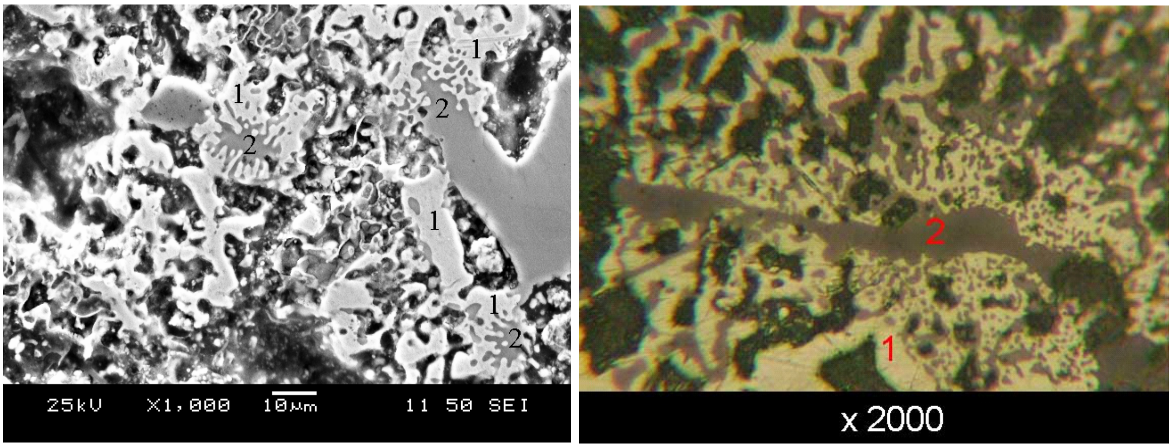

Figure 4: Structure of ferrum dititanate disintegration: 1 – metal, 2 – anosovite

Attempts of magnetic separation of the grinding products of the ore subjected to reducing roasting were not successful – every, even the smallest, particle of a powder was magnetic.

To determine a potential for the pirometallurgical separation of solid-phase reduction products a series of experiments have been conducted with several ores, different in structure and in ratio of lean material and an ore phase. A mix of ore with a reducer was formed into briquettes and stored for 1, 2 or 3 hours at 1100, 1200 or 1300°C. The received products was grinded with addition of lime and quickly melted (during 5…8 minutes).

The crystallized metal can be easily separated from slag, and there is no sweet balls of metal in the slag. Results of the electronic-spectral analysis of the metal and slag unambiguously proves the distinct separation of ferrum and titanium in the melt (fig.5).

The chemical analysis of metal showed the solid-phase reduction at all the investigated values of temperature of ferrum, chromium and phosphorus. Manganese, vanadium and titanium appears in metal only at a temperature of 1300°C. The chemical composition after 3 hours of solid-phase reduction is given in tables 2 and 3.

Table 2: The chemical composition of metal after the pirometallurgical separation of solid-phase reduction products, mass %:

Temperature of experiment, °C	C	O	P	Cr	Fe	Mn	Ti	V
1100	8,25	1,79	0,44	1,73	87,81	0	0	0
1200	9,65	1,72	0,41	3,78	84,43	0	0	0
1300	8,37	1,58	0,25	8,77	80,25	0,31	0,26	0,22

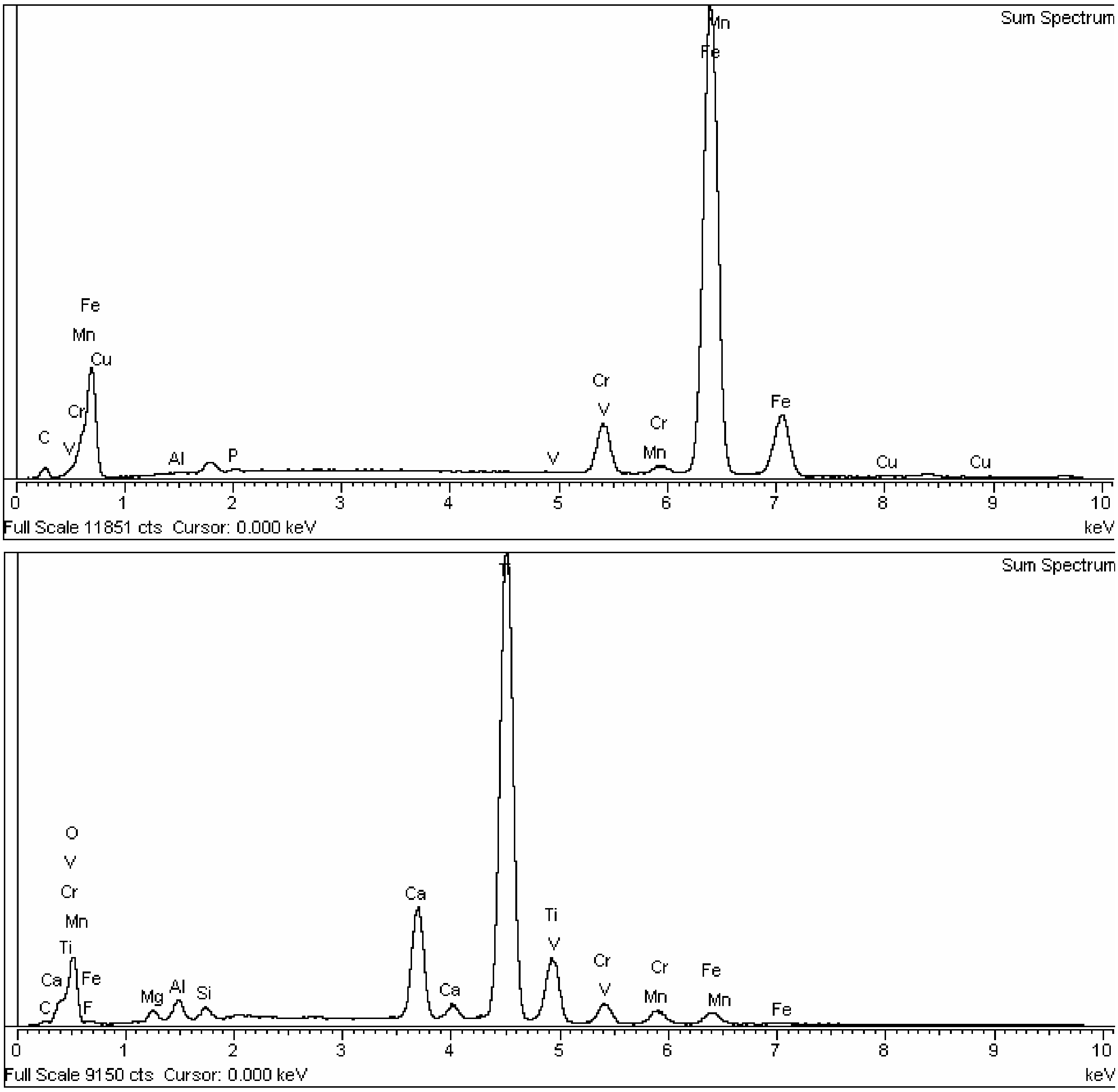

Figure 5: Power distribution of metal (above) and slag (below) after melting

Table 3: The chemical composition of slag after the pirometallurgical separation of solid-phase reduction products, mass %:

Temperature of experiment,°C	TiO_2	Cr_2O_3	FeO	MnO	V_2O_5	CaO	SiO_2	Al_2O_3	MgO
1100	65,4	5,3	10,0	2,0	0,96	9,4	2,6	2,8	1,0
1200	71,4	4,8	5,0	3,0	0,89	8,8	1,9	3,0	1,7
1300	78,4	3	1,1	2,1	0,80	9,6	1,3	2,5	1,3

Kinetic parameters of the solid-phase reduction process may be evaluated by the rate of mass change of the brickette mix of ore with reducer. According to the data presented in fig.6, and considering the metal structure the reduction of ferrum and phosphorus with all investigated values of temperature practically comes to an end within the first hour. An insignificant loss of mass with the increase in duration of exposure at temperature

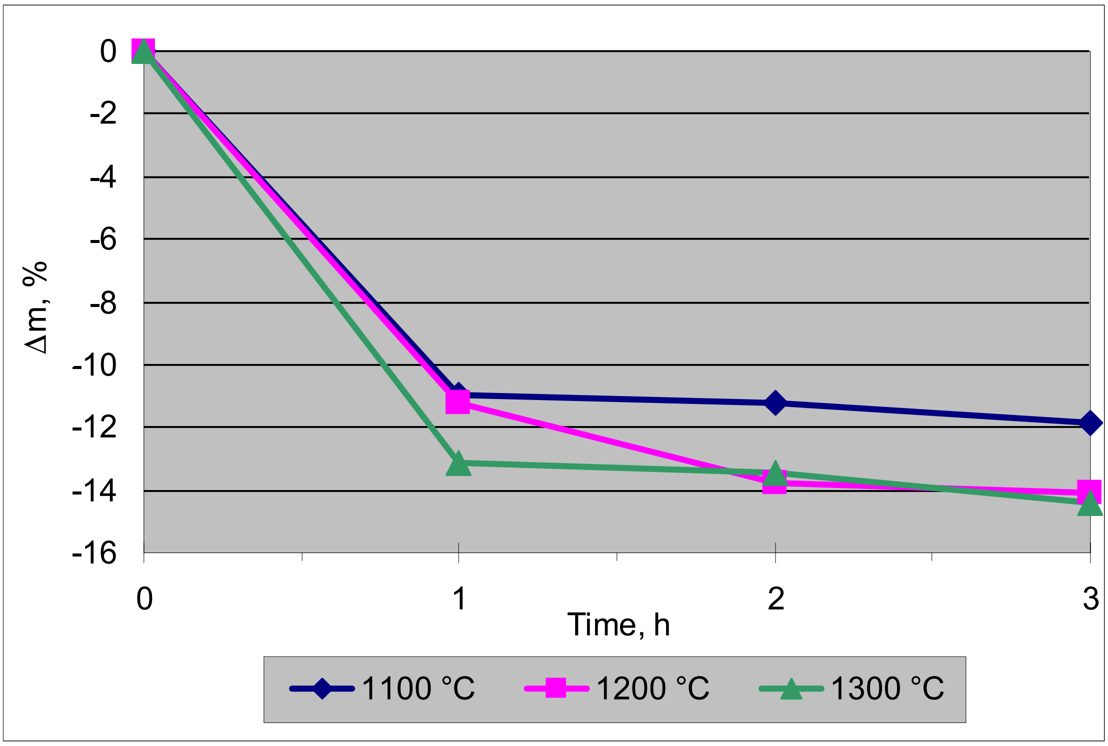

Figure 6: Mass change of the samples during isothermal exposure

of 1100 and 1200°C is apparently connected with reduction of chromium, and at temperature of 1300°C is connected with reduction of chromium, manganese, vanadium and titanium.

At the same time analysis of the solid-phase reduction process with a derivatograf[1]Q-1500D in heating conditions with a rate 15°C/min, the results of which are shown in fig.7, define higher values of temperature of the beginning of reduction of ferrum (1278°C) and of other elements (1355°C). This divergence is apparently caused by thermal inertia of samples in conditions of continuous heating.

2.2 Analysis of Experiments Results

Results of phase studies, their interactions in the initial ore and of the phases formed during thermal disintegration of the spinel solution (titanomagnetite) and as a result of the reducing process lead to the conclusion that reduction of metals from the complex titanomagnetite ore develops in the volume of a multiphase system similar to the earlier described process of metal reduction from complex chromium spinels [6-8]. On a surface of the ore lump the oxygen from oxide is withdrawn by a reducer with formation of anionic vacancies in the oxide lattice. The electrons, released at oxidation of the reducer (redundant or "defective" relative to stoichiometrical oxide) interact with the anionic vacancy with the formation of electro neutral complexes "anionic vacancy – 2 defective electrons". The redundant (defective) electrons are localized at cations possessing higher affinity to the electron and being near to the anionic vacancy. At the same time such cations are reduced either to a cation of the lower valency, or to metal condition. As a result, the complexes "anionic vacancy – 2 electrons" turn into the complexes "anionic vacancy – atom of metal" or "anionic vacancy – cation of the lowered charge". Since such atoms are connected with anionic vacancies by a condition of a local electro neutrality, then they move to the vacancy drain places together with them, forming a metal phase there.

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[1] Thermal analysis system with a simultaneous TG-DTA module

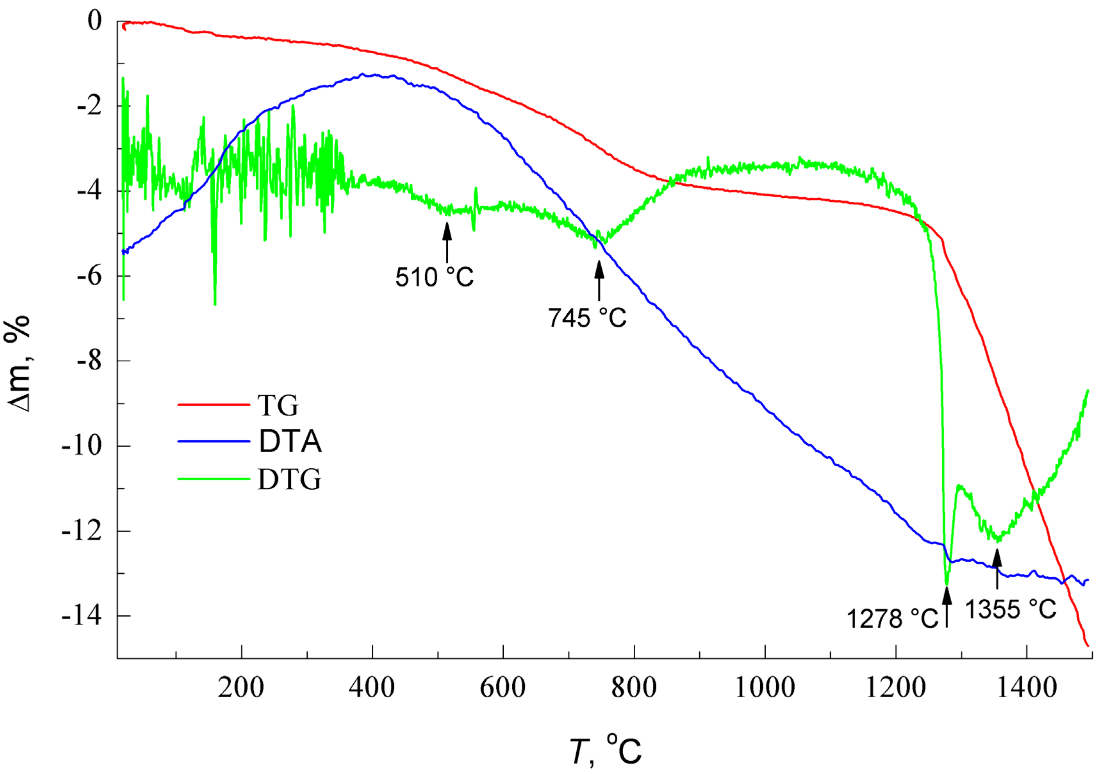

Figure 7: Results of derivatographic study of the reduction process

In titanomagnetite ore the greatest affinity to electron is possessed by cations of ferrum which are reduced to a metal condition. Cations described by smaller affinity to electron in experimental conditions are reduced only partially. It applies to chromium, manganese and vanadium which are partially reduced to a metal condition. Four-charged cations of titanium are reduced to cations of the lower charge, since the end-product of reduction of the titanium in these conditions is anosovite – the complex oxide formed by four-, three- and two-charged cations of titanium. Cations of aluminium, silicon and magnesium are not reduced and turn to a slag phase.

Since the disintegration process of the solution (titanomagnetite) and chemical compounds (ilmenite and ferrum dititanate) occurs consistently (fig. 8), the end-products – metal iron, anosovite and a "slag" phase form an extremely disperse structure. It is possible to separate a similar mix only by the pirometallurgical method. At the same time the alloyed carbonaceous product and high-titanium slag which can be used as raw material for getting alloys of titanium or titanium dioxide TiO_2 is formed.

2. CONCLUSIONS

As a result of the solid-phase ferrum reduction by carbon, the fast fusion and the liquid-phase separation of products of the solid-phase metallization it was possible to almost fully transfer ferrum into the metal phase and to fully keep titanium in the oxide phase.

The results of the conducted studies also prove that it is most advisable to derive cast-iron and high-titanium slag for their subsequent repartition to steel and titan-containing alloys in electric furnaces. Processing of the metallized titanomagnetite ore in electric furnaces is possible both with preliminary separation of ore into ferrum-vanadium and titanium concentrates, and without its separation into concentrates.

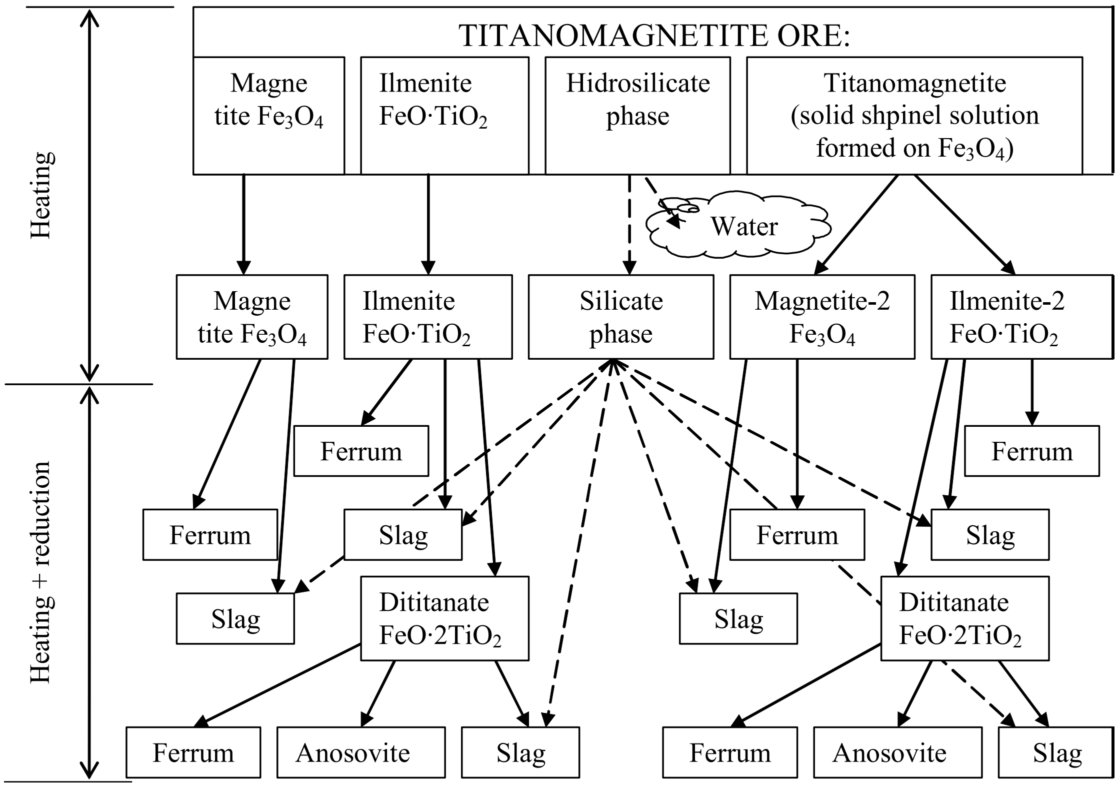

Figure 8: Diagram of structural changes in titanomagnetite ore under the influence of reducer

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