The influence of microwave radiation on the process of solid-phase recovery of ilmenite concentrate

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Abstract. A study on the effect of intensive microwave radiation on the process of solid-phase recovery of ilmenite concentrate is presented. Assessment of the degree of recovery, the change in the phase composition and elemental analysis of the reaction products were carried out by x-ray diffraction and energy-dispersive analysis. By means of electron microscopy, the dynamics of the appearance and the droplet size of the restored iron formed under the influence of microwave irradiation on the surface of solid-phase synthesis products are evaluated. High efficiency of microwave exposure on the recovery of ilmenite concentrate in the carbon medium at a temperature of 1000 °C is shown. The possibility of reducing temperature and duration of the reduction process of iron oxides in the ilmenite ore, compared with the traditional high-temperature process of enrichment of titanium ore, is established.

1. Introduction
Among the structural materials titanium and alloys on its basis are very promising and have very important advantages in comparison with other materials.

Despite large reserves of titanium in the Earth crust the cost of this construction material is large enough. This is due to the difficulty of extracting it from titaniferous raw materials presented mainly in the form of rutile and ilmenite [1–10]. Nowadays there are two technologies for recovery of ilmenite concentrate: liquid-phase, occurring in temperature intervals of 1600–1800 °C, and solid-phase which is carried out at lower temperatures which do not exceed 1000–1200 °C. In case of the solid-phase recovery, the exchange of electrons between the reducing agent and cations of metals in the oxides is carried out without melting of the ore and total removal of the oxygen from it.

Despite the fact that a solid-phase recovery is energy-wise more advantageous compared to a liquid-phase process, the recovery of iron from ilmenite ore and its disengagement in the metal phase in the temperature range of 1000–1200 °C is carried out with a fairly low speed. In this regard, there is a growing need to find new ways to speed up the process of the solid-phase recovery of iron from ilmenite concentrate to create more perfect technology of enrichment of titanium-containing raw materials.

In recent years, the use of microwave heating by processing and enrichment of metal ores is of increasing interest among researchers [11–13]. Advantages of microwave processing of materials include penetrating radiation, controlled distribution of high-frequency electric field, selective influence on the material and speed increase of the solid-state reaction [14–16]. A preliminary evaluation of economic efficiency of carbothermic recovery of metals from oxides showed that
under optimal conditions the recovery process will significantly reduce energy consumption compared with traditional methods [17–20].

2. Experimental part
The study of the effect of microwave radiation on the process of solid-phase recovery of ilmenite concentrate was carried out in the M-01 high temperature microwave with the frequency of radiation $f = 2450$ MHz. The power density of radiation during the experiment was $I = 2.5$ MW/m$^2$. For studies we prepared ore-coal briquettes consisting of ilmenite concentrate and a reductant (anthracite). The ore-coal briquettes were placed in a ceramic crucible and recovered at a temperature of 1000 °C during a specified time interval. Evaluation of the phase composition changes and the degree of recovery of the ilmenite concentrate was performed using x-ray diffractometer “Shimadzu XRD-7000”. Visualization of the products of recovery and the elemental analysis were carried out by means of “Hitachi S-3400N” scanning electron microscope with an attachment for energy-dispersive analysis of the company “Bruker”.

3. Results and discussion
The process of solid-phase recovery of ilmenite concentrate in the temperature range of 1000–1100 °C proceeds according to the following reaction:

$$(\text{FeO} \cdot \text{TiO}_2) + \text{C} = \text{Fe} + \text{TiO}_2 + \text{CO}.$$ 

The results of microscopic analysis of the reduction products of ore-coal briquettes of ilmenite concentrate in the microwave furnace are shown in figure 1.

At $t = 1000$ °C for 5 min in a microwave furnace, metallic particles with a size of 10–15 µm appeared on the surface of the concentrate. The results of energy-dispersive analysis showed that they were iron particles. The concentration of Fe in the formed drops was 90–95.9% (here and after, the weight percentage is indicated).

According to the results of x-ray phase analysis, presented in figure 2, the degree of recovery of iron in the analyzed sample was 49%.

Besides, the sample included the next phase containing unrecovered iron in addition to rutile: Fe$_2$Ti$_3$O$_9$ (Pseudorutile)—15.9%, Fe$^{2+}$TiO$_3$ (Ilmenite)—12.1%, Fe$_2$O$_3$ (Hematite)—13.8%.

When recovering ore-coal briquettes of ilmenite concentrate in a muffle without microwave exposure at the same temperature of 1000 °C for 15 min (figure 3, the degree of iron oxides recovery was close to zero and the recovery of metallic iron particles under these conditions was not observed.

The analysis of the results of firing without microwave radiation, presented in figure 3(a), showed that in a muffle furnace at $t = 1000$ °C small pores with a diameter of 200–500 nm only begin to form on the surface of the concentrate, through which later recovered iron drops begin to exude. At the same time, figure 3(b) demonstrates that already after 5 min treatment in a high-frequency electric field ($I = 2.5$ MW/m$^2$) at a temperature of 1000 °C, drops of recovered metal iron of the size of 10–15 µm are formed on the surface of ilmenite concentrate.

Thus, the results of the first experiment showed that microwave radiation allows significant intensification of the process of iron oxides recovery due to simultaneous heating the processed material inside and on its surface. The mechanism of iron oxides recovery is based on the return of the missing electrons to the metal: $\text{Fe}^{2+} + 2\text{e} = \text{Fe}^0$.

In the process under investigation, the source of the missing electrons is solid carbon. In the process of microwave irradiation, the heating of particles of coal and iron compounds is greatly intensified, which facilitates the acceleration of electron transfer from carbon to Fe$^{2+}$. Due to their smaller absorptive capacity in relation to microwave radiation, particles of titanium oxide in the ilmenite concentrate remain at a lower temperature that allows us to slow down the formation of several titanium compounds (Ti$_3$O$_5$, Ti$_2$O$_3$, TiO), formed during high-temperature
Figure 1. Microphotography of reduction products exposed to microwave radiation for 5 min.

Figure 2. X-ray diffraction pattern of the reduction products exposed to microwave radiation for 5 min.

processing of ore-coal concentrates in the temperature range from 1200 to 1500 °C and adversely affecting the quality of the enriched ore.
Figure 3. Microphotography of recovery product at the temperature of 1000 °C: (a) 15 min exposure without microwave radiation; (b) 5 min exposure to microwave radiation.

Figure 4. Microphotography of reduction products exposed to microwave radiation for 15 min.

To determine the effect of duration of microwave exposure on the process of solid-phase recovery of ilmenite concentrate, the ore-coal briquettes were placed in a microwave furnace for 15 and 30 min.
Figure 5. Microphotography of reduction products exposed to microwave radiation for 30 min.

The results of the microscopic analysis of the recovery products after 15 min of microwave exposure are shown in figure 4. The photos show that the size of the recovered iron particles increased by 1.5–2 times compared with iron particles obtained after 5 min exposure and it was 15–30 µm. The results of x-ray diffraction analysis of the reaction products showed that the degree of iron recovery made up about 51%. In addition to rutile, Fe$_2$Ti$_3$O$_9$ (pseudorutile)—12.7%, Fe$^{2+}$TiO$_3$ (ilmenite)—11.4%, Fe$_2$O$_3$ (hematite)—11.3% were detected in the sample.

A comparative content analysis of these phases after 5 and 15 min of microwave processing showed that increasing duration of high frequency radiation leads to increasing efficiency of the recovery process and decreasing concentration of Fe$^{2+}$ and Fe$^{3+}$ 2–3%. Figure 5 shows the results of microscopic analysis of the recovery products of ore-coal briquettes in the microwave for 30 min. The picture demonstrates that the size of iron particles formed on the surface of the concentrate amounted to 40–50 µm, which exceeds about 2 times the particle size of the recovered iron obtained on the surface of ilmenite concentrate after 15 min exposure. According to the results of x-ray phase analysis, the degree of iron recovery was 52%. The content of other phases in the treated sample containing unreduced iron remained almost unchanged compared with the sample subjected to 15 min exposure. The content of Fe$_2$Ti$_3$O$_9$ (pseudorutile) made—12.7%; Fe$^{2+}$TiO$_3$ (ilmenite)—10.0%, a Fe$_2$O$_3$ (hematite)—11.4%.

Table 1 demonstrates the final results of the experiments on the effect of duration of microwave irradiation with the frequency $f = 2450$ MHz and the density of $I = 2.5$ MW/m$^2$ on the degree of ilmenite concentrate recovery and the size of the formed metal particles.
Table 1. The effect of duration of microwave treatment (min) on degree of recovery (%) and size of metallic iron droplets (µm) at the temperature of 1000 °C.

| The duration of treatment | The degree of recovery | The size of droplets |
|---------------------------|------------------------|---------------------|
| 5                         | 49                     | 10–15               |
| 15                        | 51                     | 15–30               |
| 30                        | 52                     | 40–50               |

The obtained results show that increasing duration of intense microwave irradiation from 5 up to 30 min leads to increasing degree of iron oxide recovery from 49 to 52%, and the size of the particles of metallic iron formed during recovery increases from 10 to 50 µm. The fact that a similar recovery process carried out in a muffle furnace at a temperature of 1000 °C for 15 min without microwave exposure did not even allow the process of iron oxides reduction in the ilmenite concentrate to be started confirms the high significance of microwave radiation on the process of titanium ore enrichment.

4. Conclusion

The results presented in this work clearly indicate that microwave radiation allows to significantly intensify the process of iron oxides reduction in the ilmenite concentrate. Microwave exposure with frequency \( f = 2450 \text{ MHz} \) and density \( I = 2.5 \text{ MW/m}^2 \) contributes to the sharp increase in the degree of \( \text{Fe}_x\text{O}_y \) recovery from 0 to 50% even with 5 min irradiation. The increasing duration of microwave radiation up to 30 min allows large enough droplets of metallic iron to be formed on the surface of ilmenite concentrate, which can be successfully removed later by dissolution in acid solutions or by magnetic separation after preliminary mechanical grinding of the recovered concentrate.

The use of microwave processing will allow to reduce the temperature of the recovery process compared with traditional high temperature methods by 1.5–1.8 times, to reduce the time of chemical reaction, and to avoid a number of environmental problems at the stage of ilmenite concentrate enrichment.

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