Processing of mineral raw materials and production wastes by combustion under atmospheric conditions

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Abstract. The work considers the regularities of SHS of ferrotitanium, ferrochromium and synthetic mica-based fluorophlogopite. The powder mixture of minerals (silica sand, Karelian shungite, ilmenite, chromium concentrate from Shorzha) and secondary raw materials (recirculated cryolite) with metal reducing agents and KClO₄ energy additive were used for the synthesis. The regularities of the initial mixture combustion under atmospheric conditions, the synthesized product composition and structure were investigated. Low-carbon ferrochromium with carbon content of 0.2%, ferrotitanium of the composition close to that of the industrial FeTi30 and synthetic mica-fluorophlogopite were synthesized. The synthesis of porous and molten-cast materials based on fluorophlogopite is shown to be possible. The composite material of K(Na)Mg₃AlSi₃O₁₀Fe₂–MgAl₂O₄–SiC was synthesized.

1. Introduction
The aim of the research is to find optimum compositions of initial mixtures which allow using ore concentrates, mineral raw materials (quartz sand, Karelian shungite) and production wastes (cryolite) [1] as components for synthesis of target products.

The following research was carried out:
- Synthesis of ferroalloys – ferrochromium and ferrotitanium [2, 3]; the annual production output of the materials is hundreds of thousands tons in Russia;
- Synthesis of fluorophlogopites (NaMg₃AlSi₃O₁₀F₂) [4], which is used as a material of corrosion-resistant refractories working in aggressive melts of nonferrous metals (aluminum, zinc, chlorides) at $T$ up to 1373 K.

2. Experimental
The ferroalloys were synthesized by aluminothermic reduction of ore concentrates in a graphite pot of 40 mm in diameter and 60 mm in height in the air at $P = 1$ atm using the energy additive (KClO₄) according to the following chemical schemes:

$$\text{FeTiO}_3 + \text{Al} + \text{KClO}_4 \rightarrow \text{FeTi} + \text{Al}_2\text{O}_3 + \text{KCl}\uparrow$$
Cr₂O₃ + FeO + Al + KClO₄ → CrFe + Al₂O₃ + KCl↑

Chromium concentrate from Shorzha (Armenia) and ilmenite from the Crimea were used as initial materials (tables 1 and 2).

Table 1. Chemical composition of chromium-containing concentrate (mass. %)

|   | Cr  | Fe  | O    | Mg  | Si  | Al  | Ca |
|---|-----|-----|------|-----|-----|-----|----|
|   | 35.3| 13.0| 27.3 | 9.33| 4.07| 3.64| 0.5|

Table 2. Chemical composition of titanium-containing concentrate (mass. %)

| Ti | Fe  | O    | Cr, Mg, Mn, V, P, Si |
|----|-----|------|---------------------|
| 30.3| 31.0| 30.4 | 8.3                 |

Powder mixtures of quartz sand (SiO₂), Karelian shungite (table 3), metal reducing agents (magnesium, aluminum), fluorine-containing (recirculated cryolite Na₃AlF₆) and oxygen-containing components (KClO₄ is the energy additive) in accordance with the chemical schemes (a) and (b) were used to synthesize NaMg₃AlSi₃O₁₀F₂ mica.

SiO₂ + Al + Mg + Na₃AlF₆ + KClO₄ → NaMg₃(Si₃AlO₁₀)F₂ + KCl↑  
SiO₂ + Shung + Al + Mg + Na₃AlF₆ + KClO₄ → NaMg₃(Si₃AlO₁₀)F₂ + KCl↑

(a)  
(b)

Table 3. Chemical composition of Karelian schungite (mass. %)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 1. | Si | 25 |   |   |   |
| 2. | O₂ | 30 |   |   |   |
| 3. | C  | 32 |   |   |   |

### 3. Results and discussion

As a result of the research, the following compounds were synthesized:

- **ferrochromium** with iron and chromium content in the target product of 32% and 66%, respectively.

  The burning velocity of the mixtures based on chromium-containing concentrate (table 1) was 1–2 mm/s (figure 1). According to XRD analysis, the ingot consisted mainly of Cr, Fe and Al and was a solid solution of Fe–Cr (figure 2). According to EDS data, with an increase in the aluminum content in the initial mixture (from 21.5 to 28%), its content in the product increases from 0.25 to 9.0%. The content of Cr and Fe gradually decreases from 66 to 60% and from 32 to 28%, respectively.

  Metallographic analysis revealed that the structure of the ingot in the central part and at the periphery is the same. The microstructure of the alloy is represented by coarse crystals of ferrochrome solid solution separated by bright boundaries. The grain microhardness under a load of 50 g is $H_μ = 290–410$ (kg/mm²).

- **ferrotitanium** with 60% Fe, 28.2% Ti and 10% Al.

  In the experiments ilmenite from the Crimea was used (table 2). Aluminum used in the work was characterized by various dispersion degrees; the average particle size was 30 and 300 µm. The combustion regularities of the mixtures based on the ilmenite are shown in figure 3. Figure 4 shows the XRD pattern of synthesized ferrotitanium.

  Two structural components were revealed: phase based on Fe₂Ti(Fe₂AlTi), $H_μ = 750–890$ (kg/mm²) and region which is possibly Fe–Ti solid solution, $H_μ = 490–580$ (kg/mm²) under a load of 50g.
Figure 1. Influence of aluminum content on burning velocity of the mixture: $x(OC + KClO_4) + yAl \rightarrow Cr-Fe + Al_2O_3 + KCl$. OC is the ore concentrate, $x + y = 100\%$.

Figure 3. Influence of aluminum content on burning velocity of the mixture: $x(FeTiO_3 + KClO_4) + yAl \rightarrow FeTi + Al_2O_3 + KCl$, $x + y = 100\%$, 1 Al 300 µm, 2 Al 30 µm.

Figure 2. X-ray diffraction pattern of synthesized ferrochromium.

Figure 4. X-ray diffraction pattern of synthesized ferrotitanium.

- fluorophlogopite-based mica.

It is established that the main parameter affecting the burning velocity of the mixture for synthesizing fluorophlogopite is the content of potassium perchlorate in it (figure 5). XRD analysis shows that the synthesized product is a composite material based on monoclinic sodium fluorophlogopites $NaMg_3AlSi_3O_{10}Fe_2$ and $NaMg_6Al_5Si_3O_{20}Fe_4$ and contains $MgAl_2O_4$, $SiO_2$ and some amount of free silicon (figure 6). The change in the initial composition allows regulating the state of aggregation of the substance in the combustion wave from the melt to an ordinary cake. It is established that it is possible to obtain porous and melt-molded products depending on potassium perchlorate content in the initial mixture (figure 7). The microhardness of the cast product matrix, which was measured under a load of 50 g, is $H_\mu = 140–300$ (kg/mm$^2$). The material density reaches 2.57 g/cm$^3$.

The introduction of Karelian schungite into the initial composition made it possible to synthesize a composite material $K(Na)Mg_3AlSi_3O_{10}Fe_2-MgAl_2O_4-SiC$ based on fluorophlogopite. According to XRD
analysis, when SiO$_2$ was partially replaced by schungite with a particle size of less than 50 μm, the product containing silicon carbide, K-fluoroflogopite and complex Al–Mg oxide was synthesized (figure 8).

**Figure 5.** Dependence of burning velocity on potassium perchlorate content in the initial mixture: $x$(SiO$_2$ + Mg + Al + Na$_3$AlF$_6$) + $y$KClO$_4$; $x + y = 100\%$, 1 SiO$_2 < 300$ μm, 2 SiO$_2 < 50$ μm.

**Figure 6.** X-ray diffraction pattern of synthesized material.

**Figure 7.** Structure of (a) cast and (b) porous SHS-fluoroflogopite.

**Figure 8.** X-ray diffraction pattern of the synthesized composite.
4. Conclusion
According to the classification accepted in industry, the synthesized ferrochrome can be considered as a low-carbon ferrochrome with carbon content of 0.2% [5]. Ferrotitanium whose composition is close to the industrial grade FTi30, artificial mica-fluorophlogopite and $K(Na)Mg_3AlSi_3O_{10}F_2–MgAl_2O_4–SiC$ composite material are synthesized. The possibility of obtaining porous and melt-molded materials based on fluorophlogopite is shown.

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