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Special Features of Chemical and Mineralogical Composition and Technological Properties of High-Ferriferous Wocheinite

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Abstract

This paper presents the comprehensive study findings of the high-ferriferous wocheinite (a bauxite variety) of Timan deposit to evaluate the possibility of its application in the aluminosilicate ceramics production. The study was carried out by chemical, X-ray phase and thermal analysis on two samples before and after calcination. According to the obtained data, investigated material is of practical interest as a hardening and mineralizing additive to produce high-strength aluminosilicate ceramics. The strength improving ceramic structures, based on clay and bauxite raw materials mixture, is possible due to the binding of silica, which is released from the structure of kaolinite by aluminum oxide as a product of boehmite and hydrargillite dehydration to the secondary mullite.

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1. Introduction

The directed regulation of the structure and phase composition formation of silicate and oxide ceramic materials determines the possibility of obtaining ceramics with defined properties, and technology optimization allows to reduce the products cost by cutting down expenditures on high-priced raw materials ^{1,2}. In addition to the problem of increasing raw materials base for ceramic industry in Russia in recent years, problem number one for manufacture of

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ceramic materials and products is energy-efficient technology development, which in most cases is achieved by lowering the calcination temperature, without in deterioration of finished product performance properties ³⁻⁵.

Despite the increase of synthetic ceramics among the modern ceramics materials, the natural refrectory raw materials (refractory clay, kaolin, bauxite, alumina hydrates and containing the sillimanite group minerals rocks) are still very important for such traditional ceramic materials as aluminosilicate refractory, high-alumina ceramics and others^{6,7}.

Russian bauxite raw materials are characterized by high content of silica. This property is unwanted for the highalumina raw materials and, as a result, it determines the Russian bauxite as technologically low-grade stock. In addition, the high content of ferriferous additives limits its application in high-refractory ceramics production^{8,9}.

The aim of this research is to study physical, chemical and technological properties of wocheinite from the Timan deposit (the Komi Republic) as a raw material for aluminosilicate ceramics production with the different porosity.

The research was carried out on two samples of Timan Wocheinite (TW-1 and TW-2).

2. Special Features of Chemical and Mineralogical Composition

As to the grain composition of the samples (Table 1), it has been found that the Timan Wocheinite contains less then 20% of clay particles (with the size less than 5 μ m).

	content (%) of fraction (mm)							
sample code	1-0.06	0.06-0.01	0.01-0.005	0.005-0.001	< 0.001			
TW-1	37.15	39.53	6.92	6.16	10.24			
TW-2	57.04	19.68	6.36	5.48	11.44			

Table 1. Grain composition of investigated raw material (GOST 21216-81)

Chemical analysis has revealed that regarding to the chemical composition (Table 2) the both samples are high-alumina (Al₂O₃ content is more than 55%) and high-silica (SiO₂ is 2 - 3,5%) types of raw materials with the high content of ferriferous additives (Fe₂O₃ is 16-25%). These data determine wocheinite as a low-grade raw material for technical alumina and high-refractory ceramics¹⁰.

Table 2. Chemical composition of investigated raw material

sample code —	oxide content (% wt)									
	SiO ₂	Al_2O_3	TiO ₂	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O	Na ₂ O	Δm_{ign}
TW-1	9.50	51.97	2.29	22.12	0.46	0.41	1.30	0.33	0.04	11.58
TW-2	17.62	47.80	2.73	13.88	0.41	1.80	1.25	0.22	0.06	14.23



Mineralogical composition of Timan Wocheinite was evaluated by the X-ray phase analysis (Fig. 1). According to the obtained data, investigated samples are polymineral ferriferous raw materials. The main rock-forming minerals of the Timan Wocheinite are the following: alumina hydrate presented bv boehmite; ferriferous minerals mainly presented by hematite, as well as goethite and magnetite; clay mineral presented by kaolinite. Moreover, in both samples, the X-ray reflexes,

Fig. 1. X-ray diffractogram of the bauxite of Timan deposit (TW-2)

typical for boehmite, are quite intensive. It suggests that investigated wocheinite contains the significant amount of this mineral.



sample code

Fig. 2. Intensity X-ray reflections of basic minerals (kaolinite, d-0,709 nm, hematite, d-0,269 nm, and boehmite, d-0, 608 nm) on the diffractograms Timan bauxite

3. Behavior on heating

X-ray phase analysis data of Timan Wocheinite was confirmed by thermal analysis (Fig. 3). Thermogram depicts that investigated mineral contains the alumina hydrates (endothermic effect at 260 - 310 °C with weight loss from 2 to 4%), as well as the clay mineral is presented by kaolinite with a certain amount of hydrous mica. The presence of



Fig. 3. The DSC-curves of the wocheinite of Timan deposit mark TW-1

Correlation of X-ray reflex intensities of the main rock-forming minerals (boehmite, hematite and kaolinite) in the X-ray diffraction pattern of investigated samples (Fig. 2) suggests that the content of boehmite and hematite is higher in TW-1 sample than in TW-2 sample. Furthermore, TW-1 sample contains less kaolinite than TW-2 sample. These findings are correlated very accurately with chemical analysis data of the samples. Additionally, it should be emphasized that the diffraction pattern of t TW-2 sample is characterized by X-ray reflexes of calcite presence. In the chemical composition calcite is presented as CaO, the content of which is transformed to the ignited state in TW-2 sample (2.10 % wt), and it is fivefold more than in TW-1 sample (0.46 % wt).

> clay mineral and kaolinite is characteristic for TG- curve Timan Wocheinite loss of mass in the temperature range from 400 °C to 600 °C, with 65 - 75 % of total weight loss, the resulting processes dehydration clay mineral and kaolinite, which on the wave DAP are accompanied by the emergence of intensive endothermic effect with the minimum at the temperature of 530 °C - 535 °C in the DTA-curve.

> The additional endothermic effect with the minimum at 640 °C in DTA-curve of TW-2 sample and relevant to this effect weight loss in the amount of 1.5 % wt can be determined by calcium carbonate, presented by calcite in the sample diagnosed by X-ray phase analysis.

Timan Wocheinite, therefore, is a high-ferriferous wocheinite with the hematite-boehmite-kaolinite nature, content of kaolinite from 20 (TW-1) to 38% (TW-2), content of alumina hydrate (boehmite and hydrargillite) from 40 (TW-2) to 48% (TW-1) and content of additives of ferriferous minerals and rutile from 15 (TW-2) to 25% (TW-1).



Fig. 4. Sintering curves of Timan deposit bauxites (marks TW-1 and TW-2)

Analysis of the sintering process of the investigated material in the temperature range from 1000 °C to 1500 °C has shown that Timan Wocheinite is fully sintering at the temperature of 1350 °C, because of the high content of ferriferous additives. The sintering process induces the formation of quite strong structures with the compressive strength at 50-55 MPa (Fig. 4) ¹⁰.

Identification of the sintering samples phase composition was carried out by X-ray phase analysis.

Data qualitative analysis obtained by X-ray phase analysis (Fig. 5 and 6) has shown that the main high-temperature crystalline phases, which can be determined in the diffraction patterns of investigated material of the sintered samples, contain mullite, corundum, cristobalite and residual quartz.

Quantitative evaluation of the sintered samples phase composition was carried out by the combination of quantitative X-ray phase analysis and the computational method according to the chemical analysis data. Mullite, high-purity gangue quartz and technical alumina were used as standard

materials. Mullite was synthesized from pure oxides at 1650 °C. Quartz, calcined at 1600 °C, was used as the standard cristobalite. Technical alumina, calcined at 1500 °C, was used as the standard corundum. During calcination at temperatures from 100 °C to 1400 °C (Fig. 6) in the structure of both Timan Wocheinite



Fig. 5. X-ray diffractograms of Timan bauxite products of calcination in the temperature range 1100 - 1400 ° C



Fig. 6. The intensity of the X-ray reflections of mullite, corundum and quartz in the fired Timan bauxite

samples, alumina hydrates are decomposed, and as a result, corundum is formed. Also, mullite is synthesized from kaolinite and during the synthesis process of mullite amorphous silica is evolved. Amorphous silica can be partly melted and partly crystallized to cristobalite. Thus, the reduction of corundum reflex intensity with increasing temperature up to 1400 °C (especially in TW-2 sample) is most probably caused by the additional quantity of mullite synthesis due to the interaction between corundum, which is formed from alumina hydrates, and silica, which is formed from the structure of kaolinite (content of kaolinite is significantly higher in TW-2 sample than in TW-1 sample).

Furthermore, in the diffraction patterns of both investigated samples characteristic reflexes of silica were not found.

4. Conclusions

Thus, from the obtained data, it is possible to conclude that the high-ferriferous wocheinite is of practical interest as complex aluminum-containing raw material, which can be used as hardening and mineralizing additive to produce aluminum silicate ceramic materials based on the clay raw materials. The strength improving ceramic structures, based on clay and bauxite raw materials mixture, is possible due to the binding of silica, which is released from the structure of kaolinite by aluminum oxide as a product of boehmite and hydrargillite dehydration to the secondary mullite.

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