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STUDYING THE PROCESS OF PRODUCING FLUORPHLOGOPITE MELT IN ELECTRIC ARC FURNACE FOR THE PRODUCTION OF MASSIVE CORROSION-RESISTANT PRODUCTS FOR NONFERROUS METALLURGY

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ABSTRACT

The work reveals the issues of electric arc melting of nonmetallic systems, such as oxide melts, for synthesis and casting of fluorphlogopite products, which are used as corrosion-resistant hydro- and gas-tight products for conditions of elevated temperatures and aggressive effects of chlorine, ammonia, metal melts, etc. The advantages and disadvantages of arc melting furnaces with a water-cooled crucible and graphite lining in the preparation of fluorosilicate melts are revealed. The relation between melting parameters and furnace design and their effect on the structure and phase composition of fluorphlogopite casting was investigated. The rational temperature modes for producing fluorphlogopite melt were developed to minimize energy consumption and loss of volatile components from the melt. The effectiveness of using technological samples for express analysis of the fluorphlogopite casting quality is shown, which allows quickly correcting the charge composition by analyzing the technological sample fracture. Therefore, it is possible to control the melt quality and use a recycled material as charge materials in the amount of up to 50–60 % directly during melting. The proposed technological and design solutions allow producing fluorphlogopite melt in the amount sufficient for the production of massive castings over 150 kg.

KEYWORDS: electric arc melting; fluorphlogopite; stone casting; express analysis; technological samples

INTRODUCTION

Fluorphlogopite, which is produced by solidification of the melt, has the composition of natural phlogopite with the introduction of fluorine (corresponds to the formula $\text{KMg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$), is characterized by a unique combination of physicochemical properties, which is not inherent in refractory and corrosion-resistant materials used in the nonferrous metallurgy and chemical industry in chlorination and recovery processes. Fluorphlogopite material is characterized by the absence of polymorphic transformations and can be treated on metalworking equipment, the true density of cast fluorphlogopite is 2750 kg/m^3 , its compressive strength is 69.90 MPa and bending strength is 10.25 MPa, thermal expansion coefficient (0–950 °C) is $7.6\text{--}8.2 \cdot 10^{-6} \text{ deg}^{-1}$, specific volumetric electrical resistance (20 °C) is $2 \cdot 10^{10}\text{--}4 \cdot 10^{11} \text{ Ohm}\cdot\text{m}$. Moreover, its dialectical properties are preserved both

at elevated as well as at low temperatures to the level of cryogenic ones [1]. A significant advantage of cast products from conventional (sintered) refractory ones, which are produced by sintering of oxide components, is their dense cast structure without open porosity. In this case, fluorphlogopite casting as refractory compounds can operate at temperatures of 1000–1200 °C in the conditions of aggressive media for a long time and is resistant to thermal impacts. This is especially important for metallurgical and chemical furnaces operating in a constant contact with aggressive elements, such as chlorine in liquid, vapour or gaseous states. In the process of long-term operation of metallurgical chlorators and electrolyzers, the aggressive environment impregnates sintered refractory compounds, destroying a binding component, which eventually leads to the destruction of their integrity. Therefore, when using stone fluorphlogopite products in industry, it is necessary to create new furnaces, increase the service life and reduce material

and operational costs for maintenance and repair of equipment, which provides a significant economic effect [2]. However, the development of casting technology for massive products from such complex non-metallic oxide systems requires taking into account the features resulted from the composition of mineral charge components and the properties of oxide melts. During melting of fluorphlogopite melt made of mineral charge materials, the formation of melt of the base mineral (fluorphlogopite) occurs directly in the furnace. Mineral components contain volatile components (fluorine), which can be produced from the melt in the form of gaseous compounds. In addition, the viscosity of aluminosilicate melt during the formation of fluorsilicate compounds changes greatly, which can lead to significant local overheating of the melt [1]. Therefore, melting of mineral charge components and production of fluorphlogopite melt is a more complex process as to heating conditions and melting modes as compared to melting of metal alloys.

According to gas analysis, the most volatile component of the melt is hydrogen fluoride (HF). The less volatile ones include alkalis (K, Na), whose increased evaporation in the form of fluorides is associated with their relatively high mobility in the melt [2]. The volatility of individual melt components (F, K) leads to deterioration of chemical uniformity of the melt, delamination and release of high-temperature crystalline minerals (phases).

A rational approach to the synthesis of fluorphlogopite material, which should possess a certain complex of properties, can only be carried out on the basis of studies of composition-structure-properties ratios, as well as studying the impact of melting parameters on the process of producing fluorphlogopite melt.

Technological properties of fluorphlogopite melt during the melting period before its pouring into casting moulds and in the process of transition from a liquid state to a solid one are important for producing high quality castings, as the process of structure formation, formation of shrinkage and gas cavities in the castings begins in the liquid state and ends in the period of crystallisation and solidification of the melt.

RESEARCH PROCEDURE AND RESULTS

To study the features of electric arc melting of fluorphlogopite material from mineral charge components, experimental and industrial-research melts in the conditions of recovery atmosphere in flux-melting electroslag furnaces were conducted [3]. As to the design, electric arc furnaces in which the melts were carried out, are composed of a water-cooled metal or crucibles lined with graphite, electrical holder and a column with an electromechanical drive for movement of the

electrode. A moving graphite electrode is switched in the electrical circuit of the power transformer in series according to the electrode-bottom plate circuit.

The choice of a melting furnace (electric arc furnace) was determined by the features of the developed technology of manufacturing fluorphlogopite casts, which involves a periodic production of a certain amount of fluorphlogopite melt with a set chemical composition, temperature and viscosity.

The basic parameters of operating mode in melting furnaces — temperature and time are closely dependent on each other. The higher the melting temperature, the less time it takes to prepare fluorphlogopite melt. On the other hand, an increase in temperature is limited by the volatility of charge components, which requires the development of the optimum temperature mode for the melt preparation. This factor is significantly reflected in the rational choice of the required temperature mode of melting, in which the production of a high quality melt is combined with the possibility of preparing it in a set time.

The experimental melts were carried out on the research and production facilities of the PTIMA of the NASU in the flux melting furnace with a single-phase transformer of type TShS-3000-1 as a power source created at the PWI. The performance of the furnace (furnace No. 1) are given below, and its scheme is in Figure 1.

Performance of the flux-melting furnace (furnace No. 1)

Rated power, kW	138
Operating voltage, V	45
Diameter of moving electrode, mm	150
Volume of water-cooled crucible, m ³ :	
complete	0.07
operating	0.06

The furnace No. 2 was created on the base of the furnace No. 1 under the design of the LLC “ZTMK” on the base of the furnace EAF-0.5 with graphite lining of the furnace (Figure 2). An improved design of the melting furnace is intended for industrial melting and represents an electric arc single-phase furnace with graphite current-conducting bottom plate and a graphite lining. The performance of the electric arc furnace for industrial production of fluorphlogopite melt is the following:

Rated power, kW:	
minimum	160
maximum	3000
operating voltage, V	100
diameter of moving electrode, mm	150
Volume of graphite crucible, m ³ :	
complete	0.2
operating	0.17

In producing fluorphlogopite melt, both physical processes (heating of charge, melting of its compo-

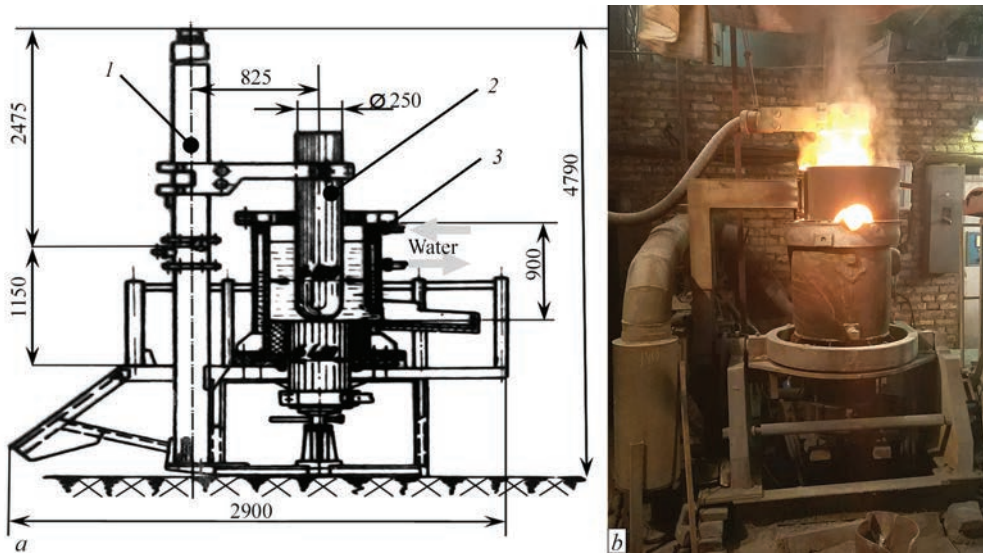


Figure 1. Scheme (a) and appearance (b) of flux-melting furnace No. 1: 1 — column; 2 — electrode; 3 — water-cooled crucible

nents, dissolution of periclase and other components in the formed liquid, evaporation of fluorides), as well as chemical reactions of decay of silicofluoride potassium,

the interaction of different components and the formation of silicates. In the renewable conditions of melting (in the presence of graphite electrode and bottom plate),

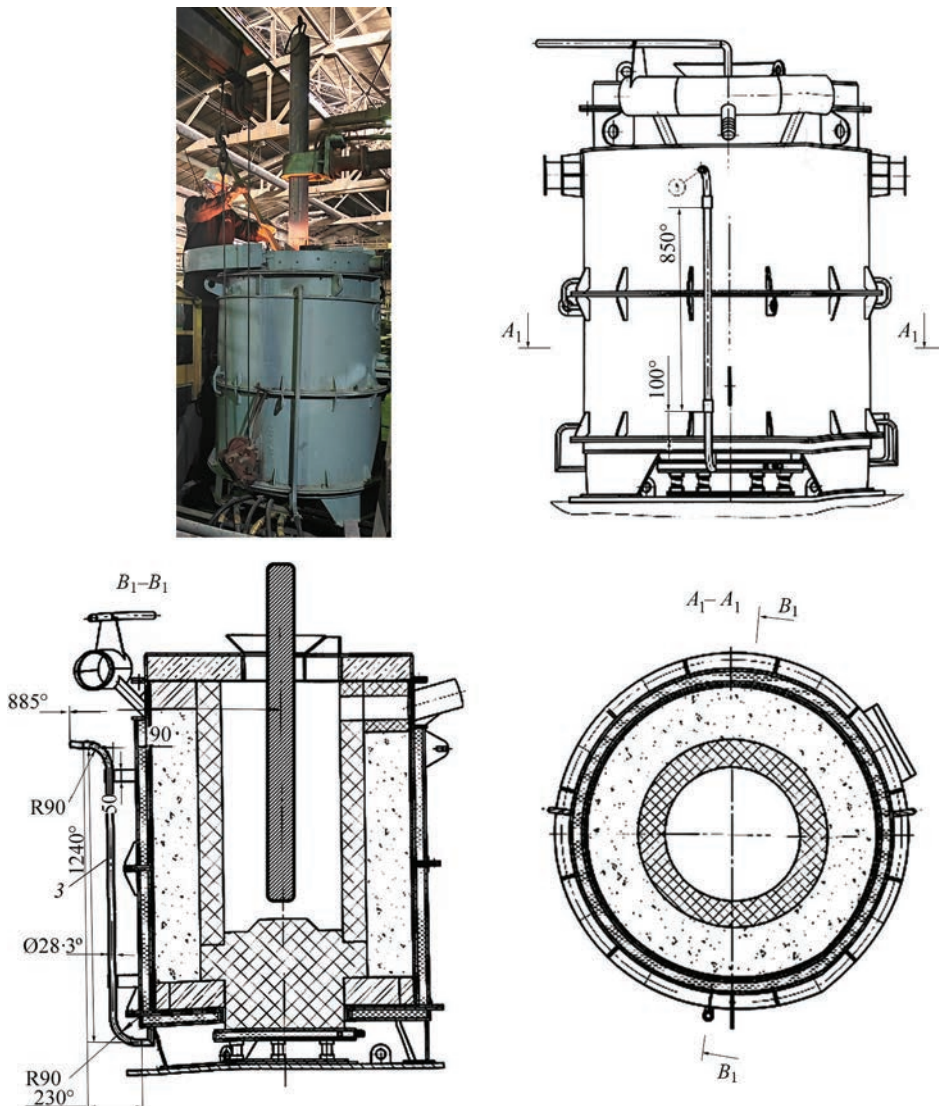


Figure 2. Appearance and scheme of electric arc furnace No. 2 for producing fluorphlogopite melt

a restoration of impurity substances (iron and manganese oxides) contained in charge materials occurs.

The process of producing fluorphlogopite melt was studied during a series of melts (mass of the melt was approximately 70 kg for each one). Analysis of the results of melts in the facilities of the PTIMA in a metal crucible showed that their temperature mode was not always satisfactory, as far as in the process of melting, a part of the melt was hardened, solidifying on the bottom plate and on a side surface of the crucible. Being a dielectric, a solidified layer of fluorphlogopite material (whose thickness at different melts ranged from 10–15 to 100–120 mm) violated electric and, accordingly, thermal modes of the furnace. The instability of the melts (furnace No. 1) is also evidenced by a relatively wide range of their duration. During melts in the metal crucible, the current values were in the range from 800 to 1400 A, and their duration was from 180 to 400 min. The analysis of power consumption during initial melts shows that in their first half the electric mode of the furnace is unstable, the power changes within a wide range (from 106 to 170 kW). Loading a cold charge at this time leads to a sharp drop of current and, accordingly, power. Thus, loading of charge and scrap at a level of melt in the furnace from 100 to 150 mm lowers the power by 30–35 kW. In the second half of melting, when the mass fraction of the melt is more than a half of the pool (from 50 to 60 % of the total weight of the melting), the thermal mode is stabilized and the loading of charge and scrap does not disturb the electrical mode of melting.

In the process of producing fluorphlogopite melt in the furnace No. 2, the duration of initial melts ranged from 60 to 63 min and the further ones lasted from 26 to 32 min. The analysis of power consumption of the following melts showed that their power mode at the beginning is comparably more stable before the first melting. The power during melts changed from 110 to 215 kW, the next melts proceeded more intensively than the initial one.

The use of graphite lining leads to a change in the nature of the melting process and shortens its duration. The use of graphite lining fostered an increase in the current of the first melt from 1100 to 1900 A, and its duration was shortened to 120–150 min. The stabilization of the melting mode is indicated by the absence of a skull on a side surface of the crucible.

Stabilization and intensification of the process during melting in the furnace No. 2 can be explained by the fact that the use of graphite lining changes the electrical and thermal modes of the melting furnace. In a metal crucible, on water-cooled walls a non-conductive skull is formed from the melt, and the electric current mainly

passes between the electrode and graphite bottom plate. In the furnace with graphite lining, no skull is formed on a side surface, and lining is heated both by heating the melt and by current. A relatively large, as compared to the area of the bottom plate, the current-conducting surface of the furnace walls and the absence of a skull on it leads to the fact that the main part of the current flows between the electrode and a side surface of the crucible [4]. This is also confirmed by the fact that an increase in the level of the melt during a constant immersion of the electrode leads to an increase in the current load, and this, in turn, provides the necessary temperature level of the melting process and contributes to its intensification.

Stabilizing and shortening the duration of melts made it possible to organize the melting process in a cyclic mode. At the same amount of produced melt, the duration of further melts ranged from 60 to 70 min. This is explained by the fact that in the initial period of further melts, the electric arc mode of operation is switched off due to the use of the initial amount of the melt of the previous melting, as well as the accumulation of heat by lining and furnace bottom plate. As a result, the consumption of electric power in the further melts is reduced and it is spent directly on the process of melting the charge, which in this case takes place at increased current loads (from 1600 to 2000 A).

However, the complexity of controlling the technological mode of melting in existing melting furnaces leads to repeated overheating and cooling of the melt in the process of its preparation (for example, when loading the next portion of the charge), as a result of which from the charge of the same composition, materials can be produced, differing by its structure and phase composition. The temperature of the melt, measured in the furnace before tapping during melting in a metal crucible ranged from 1350 to 1550 °C and with the use of graphite lining, it varied from 1550 to 1620 °C.

An increase in the temperature of the melting process leads, on the one hand, to a decrease in the duration of the melt preparation process, and on the other hand, to an increase in the number of impurity phases. When studying the process of producing fluorphlogopite melt, the influence of the temperature mode and duration of melting on the structure of the cast material was studied (Table). The optimal temperature range for the preparation of fluorphlogopite melt is 1400–1500 °C, the phase composition of the material is represented by fluorphlogopite (80–90 vol.%) and impurities: norbergite (5–10 vol.%) and glass phase (5–10 vol.%).

An increase in the melting temperature from 1500 to 1600 °C significantly reduces its duration (from 120 to 180 min), while the process of fluorphlogopite

Melt parameters and phase composition of synthesized materials, vol.%

Melt temperature, °C	Melting time, min	Fluorophlogopite	Norbergite	Enstatite	Spinel	α -cristabolite	Glass phase
1400–1450	360	80–90	5–10	–	–	–	5–10
	420	–»–	–»–	–	–	–	–»–
1450–1500	240	–»–	–»–	–	–	–	–»–
	300	–»–	–»–	3–5	–	–	–»–
1500–1600	120	75–85	–»–	5	–	–	–»–
	180	–»–	3–5	5–10	–	–	–»–
>1600	120	70–80	5	5	3–5	–	10–15
	150	60–75	–	5–10	5	5–10	–»–

formation is not significantly disturbed, although its amount slightly decreases (from 75 to 85 vol.%) and enstatite in the amount from 5 to 10 vol.% appears. A further increase in the melting temperature (above 1600 °C) slightly reduces its duration (to 150 min), but leads to a noticeable violation of the synthesis process: the amount of fluorophlogopite decreases (from 60 to 80 vol.%), the amount of glass phase (from 10 to 15 vol.%) and impurity minerals (15–25 vol.%) increases, among which alumomagnesian spinel and α -cristabolite are observed. This indicates a significant change in the chemical composition of the melt, predetermined by significant losses of fluorine — the most volatile component of fluorophlogopite melt. The losses of fluorine, as well as the formation of such impurity minerals as spinel and α -cristobalite lead to the formation of a very fine crystalline material, the macrostructure of which resembles porcelain and the size of fluorophlogopite crystals amounts to 0.3–0.5 mm.

In order to stably produce a melt with the required structure and phase composition, it is necessary to have an optimal fluorine content in the melt. Controlling the melting process by adjusting the fluorine content in the melt in a non-sealed electric arc melting furnace is problematic. At present there are no express methods to control the fluorine content in the melt [5]. The only method that allows making a quick conclusion about the content of fluorine in the melt during the melting process is the visual testing

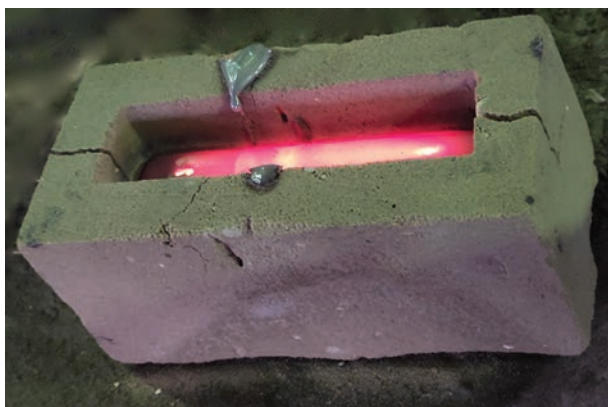


Figure 3. Appearance of a cast technological sample in a sand-clay cast mould

method, which is based on determining the structure of the material in the fracture of a technological sample (Figures 3, 4). The criteria for evaluating the sample are the following characteristics of the material fracture: color, luster, zoning, average size of fluorophlogopite crystals in the central zone of the sample. In the process of studies, it was determined that the characteristics of the structure of the castings and a technological sample are identical and do not differ from each other.

With an optimal ratio of the main components in the melt, the fracture of the sample material has the following characteristics: a uniform crystalline structure with the size of fluorophlogopite crystals of 0.5–3.0 mm, color — from light to dark gray, luster — glassy and on cleavage planes — silver (Figure 4).

Based on the studied features of preparing fluorophlogopite melt, the melting process can be conditionally divided into 2 periods: melting of the charge and formation of a set volume of melt; finishing and adjusting of the composition and temperature of the melt.

Thus, the study of the process of producing fluorophlogopite melt in electric arc furnaces showed that the intensity of meltings can be regulated by using graphite lining. The efficiency and economy of the melt preparation process increases when cyclic meltings are carried out, as well as with an increase in the power of the used transformer and capacity of the melting furnace, as far as the specific efficiency of the furnace increases.

During the first period of melting, 70–80 % of the required melt volume was deposited, then a technological sample was taken. According to the nature of the material fracture, the quality of the melt was determined and, if necessary, its composition was adjusted. The adjusting check was carried out on control samples, taken after penetration of the charge additive.

Thus, regulation of the composition of the melt during the melting period made it possible to transfer from the method of preparation based on the calculated composition of the charge to a controlled method with a periodic sampling of technological samples during the melting process and adjustment of the

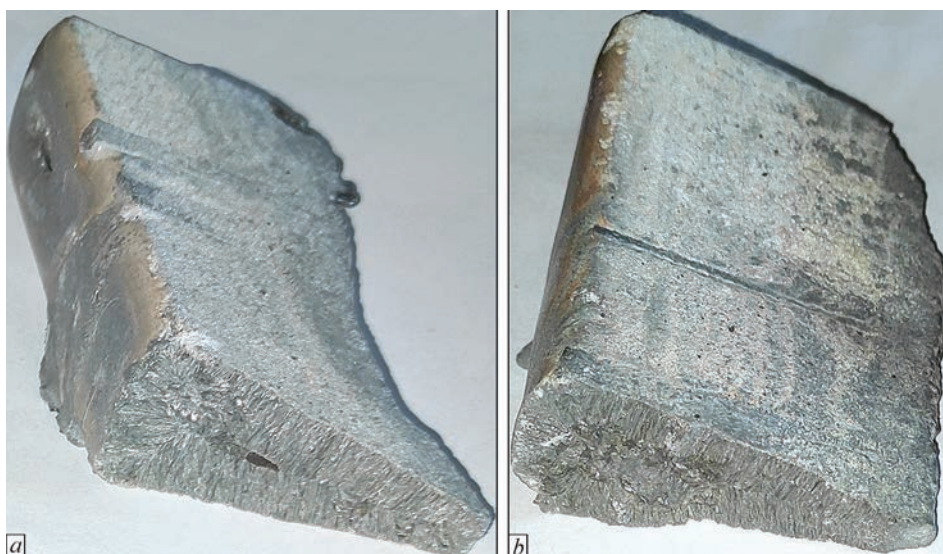


Figure 4. Appearance of the fracture of a technological sample before (a) and after (b) adjusting the composition of the fluorosilicate melt



Figure 5. Production of massive shaped fluorophlogopite castings: a — sand-clay mould; b — fluorophlogopite casting of “tap-hole stone” for chlorinator with a total weight of 150 kg

composition of the melt in order to produce a material with a stable structure and properties.

The use of an improved melting furnace and optimization of melting modes made it possible to manufacture massive (more than 150 kg) corrosion-resistant products for metallurgical furnaces of LLC “ZTMK” (Figure 5). At the same time, the cost of producing 1 ton of melt for such a casting was (based on cost, UAH: materials — 46800, electric power — 9072, salaries — 4914 for October 2021) 66686.00 UAH.

CONCLUSIONS

1. As a result of the conducted investigations, the process of producing fluorophlogopite melt in electric arc melting furnaces was studied, a method of express analysis of the quality of fluorophlogopite melt based

on the fracture of technological samples, as well as a method of adjusting the composition of the melt with the charge and wastes of fluorophlogopite casting were created.

2. The process of melting fluorophlogopite melt requires a gradual dissolution of batches of mineral charge in the deposited melt of the furnace, which leads to an increased consumption of electric power as compared to melting of metal melts in arc furnaces. Due to the use of a new melting furnace with graphite lining, as well as optimization of melting modes, the cost of producing fluorophlogopite melt was UAH 66686.00 per ton. At the same time, it was possible to reduce the share of electricity in the cost from 28 to 13%, and in absolute terms it amounted to 2700 kW·h/t.

3. It is shown that the optimal temperature for producing fluorphlogopite melt ranges within 1400–1500 °C, while the equipment and the melting mode should prevent local overheating of the melt, which leads to the loss of volatile fluorine compounds. An increase in the temperature of the process leads to a decrease in the melting time, and on the other hand, to an increase in the amount of undesired impurity minerals and a glass phase. A significant loss of fluorine by the melt results in the formation of undesirable spinel and α -cristobalite phases, which lead to the formation of a porcelain-like macrostructure of the material, which negatively affects its mechanical and functional properties.

4. The developed technology of the method of operational control of the quality of fluorphlogopite casting according to fractures of a technological sample allows using up to 50–60 % of secondary fluorphlogopite material from casting wastes and used products, which increases the environmental friendliness of production and allows saving charge materials.

5. In general, the established features of producing fluorphlogopite melt together with rational melting modes and design of melting furnaces in combination with the proposed method of express-analysis of the macrostructure of cast stone casting allow depositing the necessary amount of melt for industrial casting of massive (more than 150 kg), corrosion-resistant products for metallurgical furnaces in the conditions of electric arc melting.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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