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Processing of industrial waste by plasma-chemical method

In this paper, the results of the processing of magnesium fluoride by plasma-chemical method to obtain periclase and a solution of hydrogen fluoride (hydrofluoric acid) were presented. For the industrial implementation of plasma technologies, it is necessary to study the main parameters of plasma processes for obtaining reducing gases and processing metal oxides with them, to solve the issues of their hardware design, to increase the service life of plasma torches for their use in continuous metallurgical processes. The purpose of this work was to determine the conditions for the plasma-chemical process of processing magnesium fluoride. Thermal analysis of magnesium fluoride on a TGA/DSC2 thermogravimetric analyzer was performed. Thermogravimetric analysis showed that in the temperature range under consideration the process is endothermic, and at a temperature of ~1280°C a phase transition of the 1st kind is observed due to the melting of magnesium fluoride. The fractional composition of MgF_2 and MgO powders was studied using the Analysette-22 Nanotech laser diffraction analyzer. The results of the evaluation of the fractional composition of powders have a significant difference. At the same time, the convergence of the data obtained using laser diffraction and electron microscopy methods was found.

Keywords: industrial waste processing, plasma chemistry, magnesium fluoride, magnesium oxide, thermogravimetric analysis, granulometric composition.

Introduction

In plasma metallurgy, the processing of ores (oxides, etc.) is carried out by their thermal decomposition in plasma. A reducing agent (carbon, hydrogen, methane, etc.) or a sharp cooling of the plasma flow that violates the thermodynamic equilibrium is used to prevent reverse reactions. Plasma metallurgy allows for direct reduction of metal from ore, significantly accelerate metallurgical processes, obtain clean materials, and reduce fuel consumption (reducing agent) [1, 2]. The disadvantage of plasma metallurgy is the high consumption of electricity used to generate plasma. However, the use of low-temperature plasma makes it possible to comprehensively solve the problems of metallurgy and energy and significantly improve the environmental situation in industrial areas through the use of gaseous energy fuels and reducing agents used in blast furnace smelting and metallurgy processes. In the future the role of plasma chemical technologies will increase and will be quite profitable in industrial applications. Having a high reduction potential, plasma gases can provide elective processing of slurries of the main metallurgical processing processes, containing, in particular, non-ferrous and rare metals. Thus, the use of plasma can solve the problems of creating waste-free technologies and the shortage of raw materials in non-ferrous metallurgy [3, 4].

Beryllium is obtained by reducing beryllium fluoride with magnesium according to the technological scheme in JSC "Ulba Metallurgical Plant". In this case, the follaving reaction is carried out: $BeF_2+Mg \rightarrow MgF_2+Be$. The requirements for beryllium for use in the nuclear industry in terms of the content of impurities are of fundamental importance [5]. Beryllium fluoride BeF_2 must be of high purity, since the impurities are practically not removed during the reduction process. When conducting a reaction with a stoichiometric component ratio it is not possible to obtain a good separation of the reaction products, so a significant excess of BeF_2 is usually introduced into the charge. Good results are achieved when administered in a mixture of magnesium in an amount of only 75 % stoichiometric. Excess BeF_2 makes the slag more fusible and fluid, dissolves BeO, reduces the equilibrium amount of magnesium in the reaction mixture, and partially binds MgF_2 with magnesium fluoride. To remove slag, magnesium and intermetallic impurities from magnesium-thermal beryllium, it is subjected to vacuum melting in induction furnaces in crucibles made of beryllium oxide at a rarefaction of 133–267 Pa and a temperature of 1500–550 °C. In this case, free magnesium and beryllium fluoride evaporate, and non-volatile impurities MgF_2, VeO, Ve_2C, etc. in the form of slag float to the surface of the melt or settle to the bottom of the crucible. After this operation, the MgF_2 is filtered, washed, and sent to the dump. Thus, there is an urgent task of processing the waste of magnesium fluoride formed at beryllium production in the process of magnesium thermal reduction of beryllium fluoride and the sale of magnesium fluoride as a commercial product.

The authors of the work carry out experimental work on the processing of magnesium fluoride by a plasma-chemical method, by exposure to steam plasma to produce periclase (MgO) and capture gaseous products and to obtain a solution of hydrogen fluoride (hydrofluoric acid). For the industrial implementation of plasma technologies, it is necessary to study the main parameters of plasma processes for producing reducing gases and treating metal oxides with them, to evaluate the economic efficiency of plasma-metallurgical processes, to solve the issues of their hardware design, to increase the service life of plasma torches for their use in continuous metallurgical processes.

Experimental part

Experimental-industrial plasma-chemical plant for processing industrial waste was created on the basis of JSC "Ulba Metallurgical Plant". In the process of plasma-chemical decomposition of magnesium fluoride by ionized water vapor with the formation of solid magnesium oxide, a large amount of hydrogen fluoride gas is released, the workplace must be equipped with exhaust ventilation. Effective protection of personnel requires a set of sanitary measures: from personal respiratory protection to extensive measures to prevent air pollution. In addition, the operation of the plasma torch is accompanied by a strong whistling sound and a very bright flame of the torch. Therefore, when working a gas mask, a welding light filter and anti-noise headphones are used. Prevention of environmental air pollution involves the prevention of unorganized air escape from rooms with high pollution, as well as the cleaning of industrial and ventilation emissions.

The installation for studying the process of plasma-chemical decomposition of magnesium fluoride to produce its oxide and hydrogen fluoride consists of a plasma torch, a steam generator, a power source and a reaction chamber. For the operation of the plant, a power source of the DV-1 ore-thermal furnace with an operating voltage of 600 V was used. A plasmatron was developed and created for the plasma chemical process (Fig. 1).

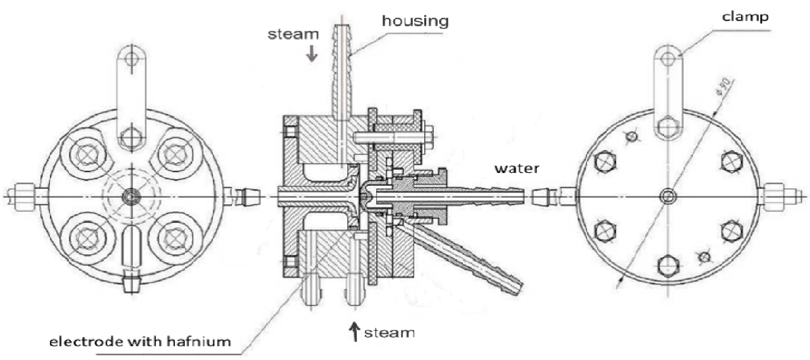

Figure 1. Assembly drawing of the plasma torch

A low-pressure steam generator (up to 2 kgf/cm^2) is manufactured to supply the plasma torch with water vapor, which provides the plasma torch with steam at a temperature of up to 130°C. During the tests, a coil for superheating steam to temperatures of about 300°C was additionally included in the design of the installation, which excludes steam condensation in the cooled areas of the plasma torch.

The dimensional characteristics of MgF_2 and MgO powders were studied using the Analysette-22 Nanotech laser diffraction analyzer (Fritsch, Germany). The device allows to determine the particle size distribution in the range of 0.01–2000 microns. The principle of operation is the diffraction of coherent laser radiation on small particles. The samples are dispersed in a liquid medium (in this case, water), and the stability of the colloid is maintained by ultrasonic treatment. Micrographs of the powders were obtained using a scanning electron microscope JSM-5610 (Jeol, Japan).

Thermal analyses were performed on a TGA/DSC2 thermogravimetric analyzer (METTLER TOLEDO, Switzerland) [6]. The sensitivity of the balance is 0.1 micrograms over the entire measurement range. The sample weight was 88.366 mg. The sensitivity of the scales is 0.1 micrograms. The experiments were carried out in the temperature range of 20-1300°C, in the atmospheric air current, at a heating rate of 10 ° per min in corundum and platinum crucibles. The phase transition heats were calculated as the area under the measured peak according to ISO 11357–1 DIN 51007.

Research results

The research resultsof the dimensional characteristics of MgF_2 and MgO powders are shown in Figures 2 and 3: each point of the integral curve Q3(x) shows how many percent of the particles have a size less than or equal to this one; each point of the histogram dQ3 (x) shows the number of particles in percent with this size. Table 1 shows the results of the study of the size distribution of microparticles.

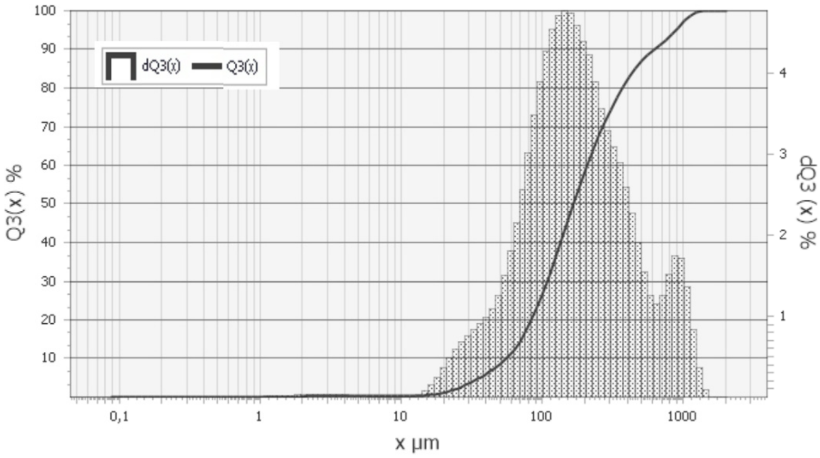

Figure 2. Size distribution of MgF_2 powder microparticles

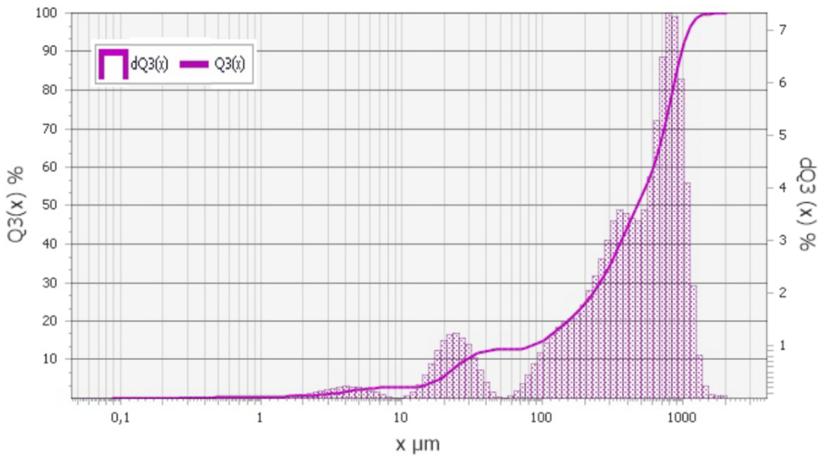

Figure 3. Size distribution of MgO powder microparticles

Table 1

Results of the particle size study

MgF_2		MgO	
Q3(x), %	X, µm	Q3(x), %	X, µm
10	55,1	10	28,5
20	84,2	20	151,4
30	109,2	30	256,8
40	135,7	40	353,6
50	167,2	50	470,6
60	208,7	60	612,1
70	269,1	70	727,8
80	368,8	80	835,9
90	617	90	968,3

As can be seen from Table 1 and Figure 3, the size distribution of MgO particles has a polymodal distribution and contains large agglomerates (Fig. 4 b, d). The obtained data coincide with the results obtained using electron microscopy (Fig. 4). It is worth noting that in the method of processing solid waste particles suspended in the plasma stream, an important parameter is the particle size of the initial substance (in our case, MgF_2), which is fed to the plasma in the form of a powder. The following processes take place in the plasma flow: heating of raw material particles to a high temperature, their melting, evaporation, chemical reactions, formation of product particles, cooling. However, there is a possibility of heterogeneous interaction of solid and liquid particles of the feedstock with the plasma, leading to the appearance of larger particles. The product may contain impurities of the starting metals and the reducing agent. This is the main disadvantage of the plasma-chemical method — a wide particle size distribution and low selectivity of the process [7]. As can be seen from Figure 2, the size distribution of MgF_2 particles is monomodal. This particle distribution does not contribute to the dense packing of the particles in the process of making MgF_2 briquettes, since the voids between the particles are filled with a binder. To solve this problem a method for manufacturing MgF_2 briquettes is being developed to improve the homogeneity of the chemical process in the plasma in the future.

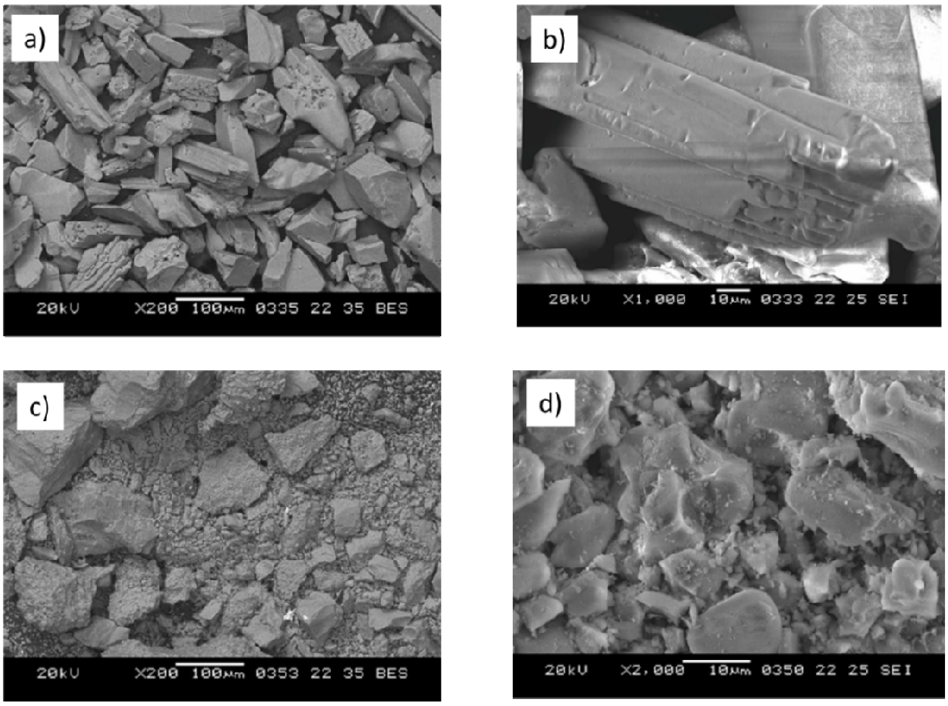

Figure 4. SEM image of powders and detailed analysis: a) and b) MgF_2; c) and d) MgO

The vapor-water plasma, depending on the temperature, consists of hydrogen, oxygen and their derivatives H, O, OH, H+, O+, O++, and electrons. This composition of steam-water plasma determines its redox character and high environmental friendliness during various plasma chemical processes. Strong intraatomic bonds, due to the small size of the hydrogen atom, determine the highest values of the enthalpy in the steam-water plasma. For example, its enthalpy at 5000 K is 7.25 times greater than the enthalpy of air with the same temperature. This determines the high rate of thermal interaction with other technological components involved in the plasma chemical process, compared to other plasmas. In addition, the steam-water plasma does not contain in its composition ballast components such as nitrogen in the air plasma, which means that the plasma chemical reactions are carried out with the highest possible thermal efficiency. The operating temperature in the low-temperature plasma jet is 5000°C or more, which makes it possible to implement a large number of high-temperature metallurgical processes. To assess the possibility of their implementation, first of all, it is necessary to perform a thermogravimetric analysis of magnesium fluoride (Fig. 5).

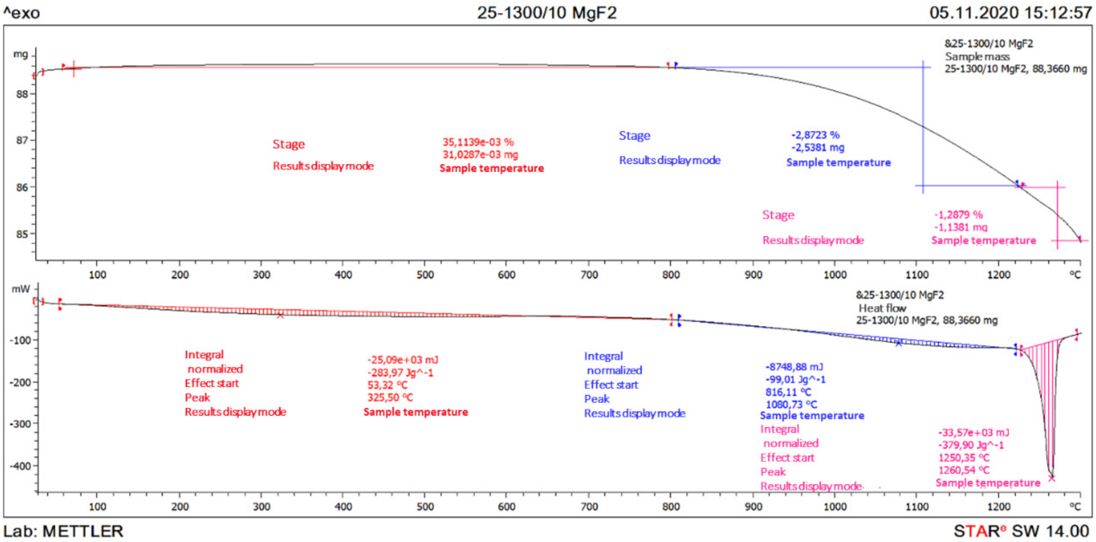

Figure 5. Results of thermogravimetric analysis of magnesium fluoride MgF_2

The thermogravimetric analysis of magnesium fluoride showed that the sample is practically stable when heated to 1080.73°C. A small gain of 0.035% can be attributed to the oxidation of magnesium fluoride when heated to 325.5°C. The sample combustion process starts at 1080.73°C and ends at 1260°C. The endothermic effect at 1260.54°C and the mass loss are associated with the melting of magnesium fluoride.

Conclusion

A pilot plasma chemical plant for processing industrial waste has been created. The installation for studying the process of plasma-chemical decomposition of magnesium fluoride to produce its oxide and hydrogen fluoride consists of a plasma torch, a steam generator, a power source and a reaction chamber. Aplasmatron was developed and created for the plasma chemical process. The condition of the plasma-chemical process of processing magnesium fluoride is determined. Thermogravimetric analysis has shown that the process temperature range under consideration is endothermic, i.e., its implementation requires an external heat supply, and the combustion process of magnesium fluoride begins at 1080.73°C and ends at 1260°C. On the basis of the conducted experimental studies aimed at studying the granulometric composition of the initial MgF_2 powder, it was found that the particle size distribution has a monomodal character and contains large agglomerates. This can lead to incomplete recycling of magnesium fluoride waste into magnesium oxide of low-temperature and high-temperature modifications.

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Өндірістік қалдықтарды плазмохимиялық әдіспен өңдеу

Мақалада периклаз және фторлы сутегі (плавик қышқылы) ерітіндісін алу мақсатында магний фторидін плазмохимиялық тәсілмен қайта өңдеу бойынша нәтижелер ұсынылды. Плазмалық технологияларды өнеркәсіптік іске асыру үшін қалпына келтіру газдарын алудың және олармен металл оксидтерін өңдеудің плазмалық процестерінің негізгі параметрлерін зерттеу, оларды аппаратуралық ресімдеу, үздіксіз металлургиялық процестерде қолдану үшін плазмотрондардың жұмыс ресурсын арттыру мәселелерін шешу қажет. Бұл жұмыстың мақсаты магний фторидін өңдеудің плазмохимиялық процесінің шарттарын анықтау. Магний фторидіне термиялық талдау TGA/DSC2 термогравиметриялық анализаторында жүргізілді. Термогравиметриялық талдау қарастырылып отырған температура диапазонында процесс эндотермиялық және ~1280 С температурада магний фторидінің еруіне байланысты 1-ші типтегі фазалық ауысу бар екенін көрсетті. MgF_2 және MgO ұнтақтарының фракциялық құрамы Analysette-22 Nanotech лазерлік дифракциялық анализаторында зерттелген. Ұнтақтардың фракциялық құрамын бағалау нәтижелері айтарлықтай айырмашылыққа ие. Бұл жағдайда лазерлік дифракция және электронды микроскопия әдістерін қолдану арқылы алынған мәліметтердің ұқсастығы анықталды.

Кілт сөздер: өнеркәсіптік қалдықтарды қайта өңдеу, плазмохимия, магний фториді, магний оксиді, термогравиметриялық талдау, гранулометриялық құрам.

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Переработка промышленных отходов плазмохимическим способом

В статье были представлены результаты по переработке фторида магния плазмохимическим способом с целью получения периклаза и раствора фтористого водорода (плавиковой кислоты). Для промышленной реализации плазменных технологий необходимо исследовать основные параметры плазменных процессов получения восстановительных газов и обработки ими оксидов металлов, решить вопросы их аппаратурного оформления, повышения ресурса работы плазмотронов для применения их в непрерывных металлургических процессах. Целью данной работы являлось определение условия проведения плазмохимического процесса переработки фторида магния. Проведен термический анализ фторида магния на термогравиметрическом анализаторе TGA/DSC2, который показал, что в рассматриваемом диапазоне температур процесс является эндотермическим, и при температуре ~1280 ˚С наблюдается фазовый переход 1-го рода, обусловленный плавлением фторида магния. Фракционный состав порошков MgF_2 и MgO исследован на лазерном дифракционном анализаторе Analysette-22 Nanotech. Результаты оценки фракционного состава порошков имеют существенное различие. При этом обнаружена сходимость данных, полученных с использованием методов лазерной дифракции и электронной микроскопии.

Ключевые слова: переработка промышленных отходов, плазмохимия, фторид магния, оксид магния, термогравиметрический анализ, гранулометрический состав.

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