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Assessment of thermodynamic parameters of the plasma chemical process for magnesium oxide production

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This work are presented the calculation results of thermodynamic parameters of the reaction of magnesium fluoride decomposition by ionized water vapor with the formation of solid magnesium oxide and gaseous hydrogen fluoride at atmospheric pressure in the temperature range from room temperature to 2800°C . The calculation of the thermodynamic parameters was carried out with the Reaction Equations software module of scientific programs HSCChemistry package. Thermodynamic analysis of magnesium fluoride MgF_2 was carried out on a thermogravimetric analyzer TGA/DSC2. The thermodynamic parameters results are in good agreement with the results of thermogravimetric analysis. There were determined the optimum conditions for plasma-chemical processing of magnesium fluoride.

Keywords: plasma-chemistry; magnesium fluoride; magnesium oxide; thermodynamic parameters; thermogravimetric analysis

Introduction

One of the most important directions at present is the development of wasteless and low-waste resource-saving technological processes that provide full and comprehensive use of raw materials, saving material and energy resources, waste recycling [1]. One way to solve the waste recycling problem is to use the plasma-chemical method [2-4], i.e. the chemical method of obtaining highly dispersed powders of nitrides, carbides, borides, and oxides, which consists in a reaction in a low-temperature plasma away from equilibrium at high nucleation rate of new phase and low growth rate of nuclei. The advantage and peculiarity of this method is the high energy content of heat flow (the temperature of plasma heat carriers reaches $\approx 10^4$ K, their enthalpy values are 100–200 kcal/mol), which provides a large specific capacity of the equipment. Because of this, the use of plasma chemistry is appropriate for the implementation of endothermic processes, such as obtaining oxides from salt solutions that require high energy consumption. Such a process does not require the use of chemical precipitant reagents, as a result, the volume of discharged solutions is minimized [5-7]. It is important that chemical transformations in nonequilibrium plasma can be carried out predominantly by a single dedicated mechanism. In this case, varying the plasma parameters makes it possible to control the chemical process, directing it through the desired channel, and optimize its energy efficiency.

Beryllium is a very important metal in production because it is used in nuclear weapons and reactors, aircraft and spacecraft structures, instruments, X-ray installations, mirrors and other industries [8]. An important source of reducing the cost of beryllium production is to increase the extraction of beryllium by involving beryllium-containing waste in the processing. To involve secondary beryllium and beryllium-containing waste in the processing, a research cycle was conducted aimed at developing technologies for safe dissolution of waste, obtaining hydroxide and oxide, fluoride and beryllium metal of high quality. Methods of dissolution of beryllium in various media are widely described in the literature: solutions of alkalis, acids, fluoride salts [9]. The disadvantage of these methods is the high fire explosion hazard associated with the release of hydrogen. Electrochemical dissolution is based on the method of anodic dissolution of metal [10]. Solutions of sodium or ammonium sulfates are used as an electrolyte. The disadvantage of this method is a significant release of ammonia during electrolysis and subsequent boiling of the solution, high power consumption, as well as low process performance. The most common method of obtaining beryllium metal is the magnesium thermal reduction of beryllium fluoride. Beryllium fluoride forms a molten slag with MgF_2, dissolving beryllium oxide from the surface of the reduced metal particles. At this moment, JSC "Ulba Metallurgical Plant" has accumulated about 2000 tons of magnesium fluoride MgF_2 in beryllium production [11]. Thus, it is an urgent task to recycle magnesium fluoride waste generated at beryllium production during magnesium thermal reduction of beryllium fluoride and to sell magnesium oxide as a commercial product. Plasma-chemical process allows to organize a closed cycle of fluorine and to use obtained magnesium oxide as a refractory. In this regard, the purpose of this work is to estimate the thermodynamic parameters of magnesium fluoride decomposition reaction by ionized water vapor to determine the optimal conditions for the plasma-chemical process of industrial waste recycling.

Calculation of thermodynamic parameters of the plasma chemical process for magnesium oxide production

It is known that low-temperature water vapor plasma is not only a heat transfer medium, but also an active reagent in physical and chemical reactions. Due to its unique properties in terms of enthalpy, environmental friendliness, wide availability, steam-water plasma is promising in technological processes of metallurgy, power engineering, mechanical engineering, plasma chemistry.

Depending on the temperature, steam-water plasma consists of hydrogen, oxygen and their derivatives: H, O, OH, H^+, O^+, O^{++} and electrons. Such composition of steam-water plasma determines its redox character and high environmental friendliness in various plasma-chemical processes.

Strong intra-atomic bonds, due to the small size of the hydrogen atom, determine the highest values of enthalpies in the vapor-water plasma. For example, its enthalpy at 5000 K is 7.25 times higher than the enthalpy of air at the same temperature. In comparison with other plasmas, this determines the high rate of thermal interaction with other technological components involved in the plasma chemical process. In addition, steam-water plasma does not contain ballast components such as nitrogen in air plasma, which means that plasma-chemical reactions proceed with the highest thermal efficiency possible. The operating temperature in the jet of low-temperature plasma is $5000^{\circ}C$ and more, which allows the implementation of a large number of high-temperature metallurgical processes [12].

First of all, it is necessary to calculate the thermodynamic parameters of the chemical process to be implemented and choose the optimal range of these parameters for it to assess the possibility of their implementation. In this work we consider the possibility of decomposition of magnesium fluoride by ionized water vapor with the formation of solid magnesium oxide and gaseous hydrogen by reaction (1):

$$MgF_2 + H_2O \rightarrow MgO + 2HF, \tag{1}$$

The calculation of thermodynamic functions (molar heat capacity of enthalpy, entropy, Gibbs energy) during a chemical reaction was performed as follows. Standard values of enthalpy H_{298}, entropy S_{298}, and coefficients of polynomials A, B, C, D, by which the value of molar heat capacity at an arbitrary temperature T is calculated in accordance with expression (1), are stored in a database for calculation of thermodynamic functions characterizing an individual substance. The enthalpy of an individual substance at a temperature T that differs from the standard temperature of 298 K is calculated according to formula (2):

$$H_T = H_{298} + \int_{298}^{T} C_p \cdot dT + \sum H_{\phi}, \tag{2}$$

where H_{298} – the enthalpy value of a given substance under standard conditions; C_p – the molar heat capacity; ΣH_{ϕ} – the enthalpy of phase transitions (polymorphic transformations, melting, evaporation). The value of entropy is defined as

$$S_T = S_{298} + \int_{298}^{T} \frac{C_p}{T} \cdot dT + \frac{\sum H_\phi}{T}, \tag{3}$$

where S_{298} – the entropy value of a given substance under standard conditions; C_p – the molar heat capacity; $\frac{\Sigma H_\phi}{T}$ – the entropy of phase transitions (polymorphic transformations, melting, evaporation).

The Gibbs energy for a given substance is calculated by formula (4)

$$G_T = H_T - TS_T, \tag{4}$$

The main difficulty in calculating of the thermodynamic characteristics of matter at an arbitrary temperature is the calculation of temperature corrections in the form of integrals in expressions (2) and (3). Approximate calculation methods, such as the Temkin-Schwartzman method, were used earlier to simplify computational procedures without the use of a computer. However, in this regards the calculation was a rather long routine sequence of calculations and implied the need to refer to reference data, which were borrowed from the literature. Since the algorithm for calculating thermodynamic functions is known and is the same for any substances, the calculation of parameters was performed in the Reaction Equations program module of the HSCChemistry [13, 14] of scientific programs package.

The calculation of changes in thermodynamic parameters in the course of a chemical reaction is an actual and frequently encountered problem, the solution of which allows us to answer a number of practically important questions. The sign of the change in the Gibbs energy allows us to judge the possibility of spontaneous implementation of the reaction in a certain direction. The value of the change in enthalpy, which is numerically equal to the heat effect of the reaction and opposite in sign, informs us whether the reaction in question is exo– or endothermic, whether it releases energy or absorbs it from the external environment. The value of the equilibrium constant allows us to determine the equilibrium composition at a given initial composition of the system in which the reaction occurs. The thermodynamic parameters of the reaction considered (1) at atmospheric pressure in the temperature range from room temperature to 2800°C are shown in Figures 1–4.

Thermogravimetric analysis of magnesium fluoride

Thermal analyses were performed on a TGA/DSC2 thermogravimetric analyzer (METTLER TOLEDO, Switzerland). The sensitivity of the scales was 0.1 μg over the entire measurement range. The mass of the sample was 88.366 μg. Sensitivity of the scales – 0.1 μg. Experiments were performed in the temperature range 20°C – 1300°C, in atmospheric air current, at a heating rate of 10° /min in corundum and platinum crucibles. Phase transition heats were calculated as the area under the measured peak according to the norm of ISO 11357-1 DIN 51007. The results of thermodynamic parameters are in good agreement with the result of thermogravimetric analysis (Figure 5).

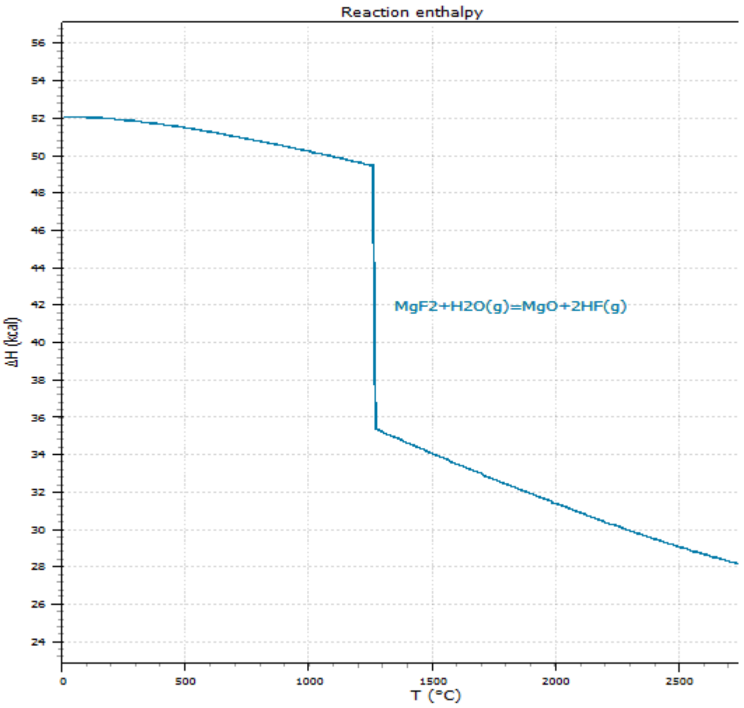

Figure 1. Enthalpy change of ΛH process from reaction temperature.

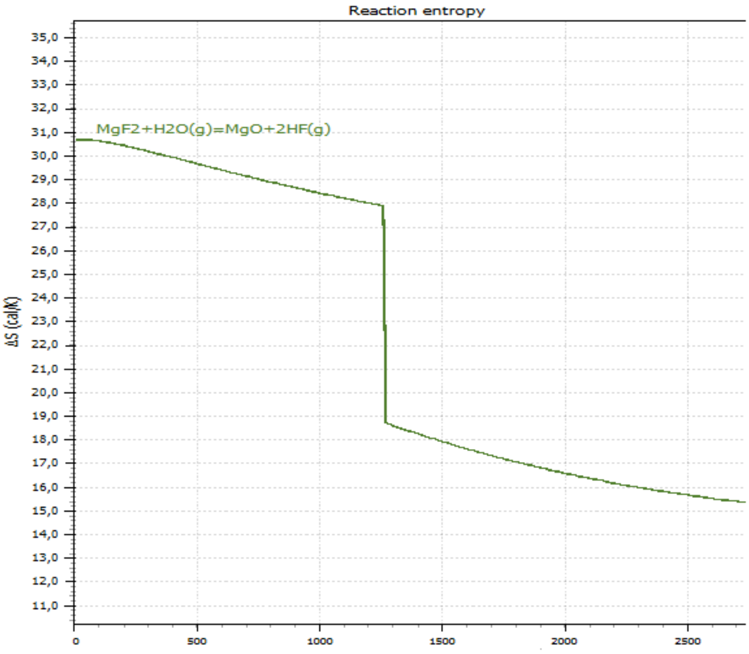

Figure 2. Enthalpy change of ΛS process from reaction temperature.

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

The analysis of the obtained calculations shows:

– the process is endothermic in the considered temperature range, i.e. heat

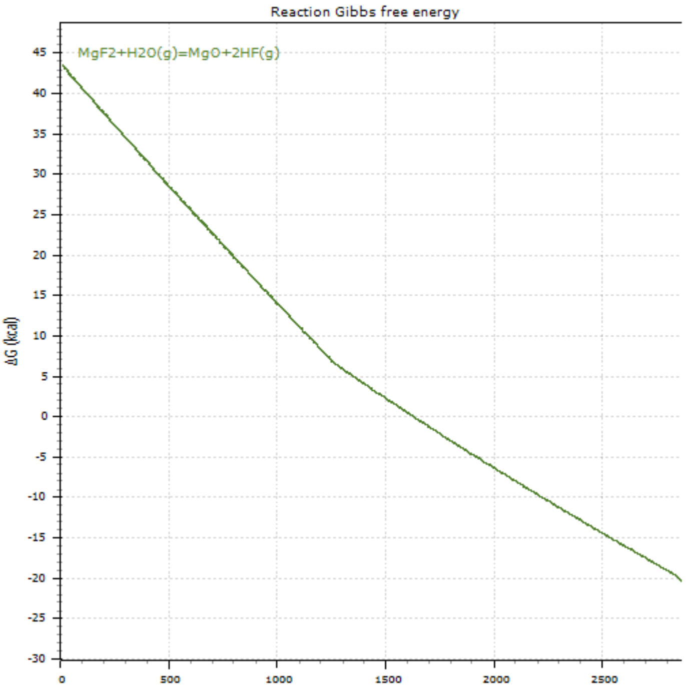

Figure 3. Gibbs enegrgy change of ΛG process from reaction temperature.

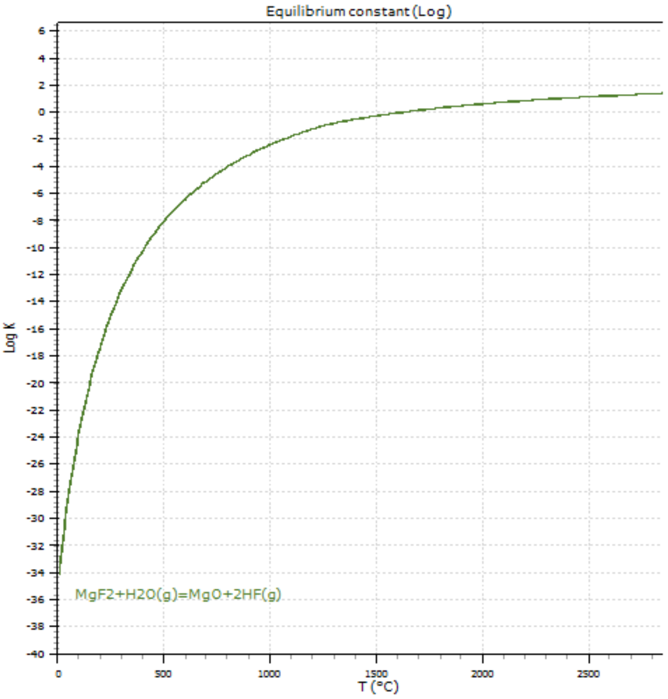

Figure 4. Change in the value of the equilibrium constant of K process from the reaction temperature.

supply from outside is required for its realization;

– the phase transition of the first type due to magnesium fluoride melting is observed at temperature $\approx 1280^{\circ}\mathrm{C}$;

– it is possible to react from left to right above temperature $\approx 1650^{\circ}\mathrm{C}$ thermodynamically, i.e. the formation of magnesium oxide and hydrogen fluoride;

– the process temperature must be maintained at more than $3000^{\circ}\mathrm{C}$ $(\mathrm{LogK} \to)$ for the reaction to be sufficiently complete.

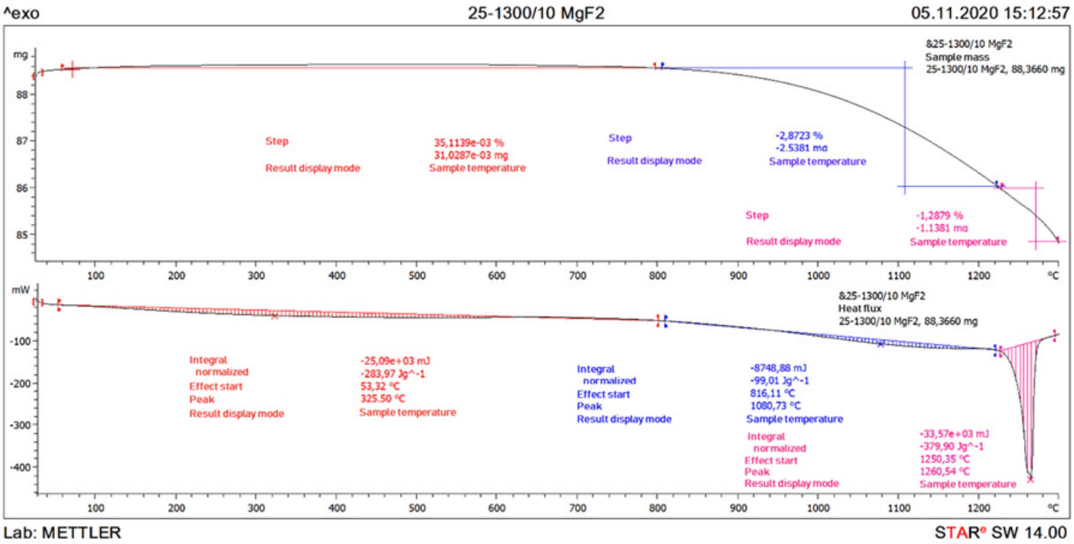

Figure 5. The result of thermogravimetric analysis of magnesium fluoride MgF_2 .

Conclusion

This work was determined the optimal conditions for the plasma chemical process of magnesium fluoride processing. Calculation of parameters was performed in the program module Reaction Equations of package of HSCChemistry scientific programs. The analysis of the obtained calculations shows: the process is endothermic in the considered temperature range, i.e. heat supply from outside is necessary for its realization; the phase transition of the first type is observed at $\approx 1280^{\circ}C$, which is caused by magnesium fluoride melting; reactions with the formation of magnesium oxide and hydrogen fluoride are possible thermodynamically above the temperature of $\approx 1650^{\circ}C$; temperature needs to be kept on more than $3000^{\circ}C$ $(\mathrm{LogK} \rightarrow)$ for a quite complete reaction the process. The results of thermodynamic parameters are good in agreement with the result of thermogravimetric analysis.

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