

STUDYING ISOTOPIC COMPOSITION OF PLASMACHEMICAL CONVERSION PRODUCTS OF SULFUR HEXAFLUORIDE

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The results of investigation of sulfur hexafluoride decomposition in mixture with hydrogen and oxygen in plasma of pulsed electron beam formed by accelerator TEA-500 (350...500 kV, 60 ns, current density 0,3...0,4 kA/cm²) have been presented. The data of thermodynamic simulation of gas mixture SF₆+O₂ and SF₆+H₂+O₂ conversion in low-temperature plasma and gas mixture composition after electron beam influence measured by mass-spectrometer are given. It is shown that the formed gas-cycle compound synthesized in plasma of pulsed electron beam is sulfur difluoride-oxide. Isotope analysis of (SOF)⁺ and (SOF₂)⁺ ions is carried out. It is obtained that sulfur isotope ³⁴S content in sulfur difluoride-oxide exceeds its content in initial sulfur hexafluoride in 1,8±0,1 times.

Introduction

Recently, the interest to chemical and physical properties of substance stable isotopes has increased. Different physical and chemical processes are used for their obtaining. The main separation method (with centrifuges) requires expensive equipment and long time for obtaining high degree of enriching. Therefore, the development of new techniques of obtaining isotopes is actual. In the paper [1] more than 30-fold enriching with isotope ¹⁵N of nitrogen atoms in afterdischarge zone of pulse charge in nitrogen flow was revealed experimentally. To explain this effect the model of two-stage enriching with isotope ¹⁵N of high vibrational levels of electron-excited state of N₂ with further dissociation of this state was suggested.

Fluoride compounds are widely used in technological production limits of rare-earth metals, isotope separation [2]. Metal is reduced from fluoride compound at heating fluoride mixture with hydrogen; this process requires the most power inputs at obtaining pure metal. The process of hydrogen reduction of fluoride compounds causes efficiently also in plasma-chemical processes allowing decreasing significantly energy expenditures due to the absence of heating reactor and gas-phase mixture up to high temperature. Besides, the conditions implemented at gas mixture pulse excitation with electron beam are profitable for organizing chain chemical processes. In these conditions not only energy of excitation source but also chemical energy of initial agent mixture is consumed for obtaining required products [3, 4]. Efficient excitation of molecule vibrational levels occurs also in plasma of pulse electron beam therefore isotope effect display is possible at fluoride compounds conversion.

The aim of the given paper is to study isotope composition of conversion products of fluoride compounds in plasma of pulse electron beam. Sulfur hexafluoride was chosen as the initial compound. Natural sulfur consists of four isotopes: ³²S (95,1 %), ³³S (0,74 %), ³⁴S (4,16 %) и ³⁶S (0,016 %). High concentration of ³⁴S allows tracing the change of isotope composition at conversion of sulfur containing compounds by universal mass-spectrometer having low mass resolution.

1. Experimental device

Experimental researches in sulfur hexafluoride decomposition were carried out at specialized pulse elec-

tron accelerator TEA-500 [5]. Electron kinetic energy amounted to 350...500 keV, total electron energy per one pulse was equal 90 J in the given experiments. Pulse duration at half-height was equal to 60ns, beam diameter was 5cm, electron current density at the reactor input did not exceed 0,4 kA/cm². Electron beam was injected to the closed reactor through anode foil (Al, 130 mkm) from the end. Reactor is the cylinder of stainless steel with inner diameter of 14 cm and volume of 3l. Composition of gas original mixture in the reactor and after the influence of pulse electron beam was measured by mass-spectrometer MX-7403. Output signal of mass-spectrometer was transmitted through ADC «Lan-7» with galvanic separation to the computer. Changes in content of gas mixture components were estimated by changing the area of corresponding mass-spectra peak.

To determine isotope composition of the original mixture and processing products the gas chromatograph-mass-spectrometer TRACE DSQ was used. It is intended for studying molecular composition of complex organic and inorganic compounds having boiling temperature lower than 500 °C. The distinctive feature of the device is high sensitivity allowing defining substances with content from 1 mkg/l in the range of 1...1050 amu.

2. Thermodynamic modeling of sulfur hexafluoride conversion

To control the change of isotope composition at conversion of SF₆ it is necessary to obtain gas-phase products which can be analyzed by mass-spectrometer. Before the experiments thermodynamic modeling was carried out for determining optimal composition of gas original mixture allowing synthesizing gas-phase sulfur containing compounds in appreciable quantities. The most suitable products of SF₆ conversion are sulfur dioxide and sulfur difluoride-oxide. They are in gas phase at room temperature, have low reactivity, lines of their mass spectrum are not overlapped with lines of sulfur hexafluoride mass spectrum.

Low-temperature plasma was computed using automated system of thermodynamic calculations «TERRA» [6]. Calculations were carried out for the temperature range of 300...5000 K and original mixture pressure 0,1 MPa. Values of equilibrium molar concentrations of chemical compounds (in mole per kg of original gas mix-

ture) the formation of which in the given conditions is thermodynamically impossible were the final result of computation. The diagrams of dependences of mole concentrations of forming chemical compounds of the studied system on temperature were plotted on their basis.

The results of calculations of sulfur hexafluoride conversion in the mixture with oxygen are given in Fig. 1. It was obtained that at thermal decomposition of mixture $\text{SF}_6 + \text{O}_2$ at change of oxygen concentration in the mixture from 2 to 10 % sulfur dioxide is not formed.

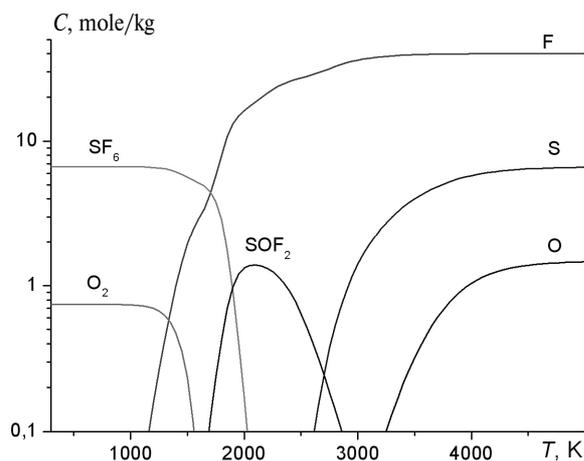


Fig. 1. Dependence of mole concentrations of substances forming in low-temperature plasma SF_6 and O_2 . Original mixture (in kPa): 90 $\text{SF}_6 + 10 \text{O}_2$

The carried out calculations showed that sulfur difluoride-oxygen is the main product of sulfur hexafluoride conversion in the mixture with oxygen and hydrogen at oxygen content lower than 30 rev. %. A part of calculations is presented in Fig. 2.

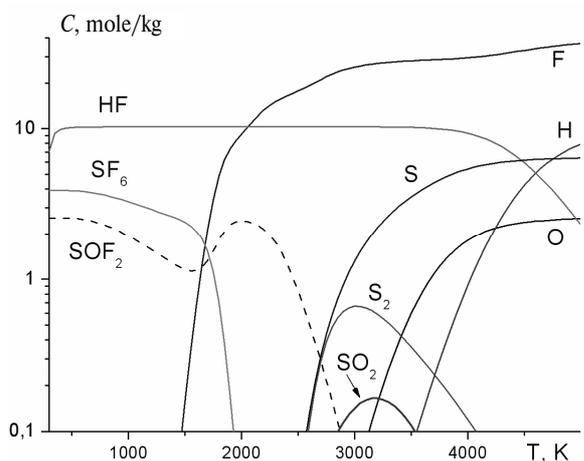


Fig. 2. Dependence of mole concentrations on substances forming in low-temperature plasma of sulfur hexafluoride in the mixture with oxygen and hydrogen. Original mixture (in kPa): 50 $\text{SF}_6 + 40 \text{H}_2 + 10 \text{O}_2$

Thermodynamic calculations showed that at low concentration of oxygen in the original mixture the main decomposition products of sulfur hexafluoride are hydrogen fluoride and sulfur difluoride-oxygen. Sulfur dioxide is formed at temperature lower than 3500 K and at temperature lower than 2800 K it is turned into sulfur

difluoride-oxygen. Hydrogen fluoride has high reactivity and reacts with the material of plasmachemical reactor therefore, it was not revealed in conversion products. At oxygen content in the original mixture more than 30 rev. % the main product of sulfur hexafluoride conversion is sulfur difluoride-oxygen.

3. Studying product composition of SF_6 conversion in electron beam plasma

The survey spectrum of $\text{SF}_6 + \text{H}_2 + \text{O}_2$ conversion products in plasma of pulse electron beam (after 150 pulses) is given in Fig. 3. The data of two tests of gas mixture in the reactor are given. Gas mixture composition in the reactor was measured by mass-spectrometer MX-7403.

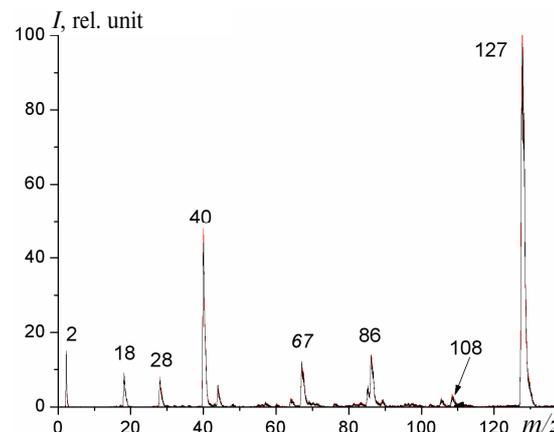


Fig. 3. Survey mass-spectrum of decomposition products of the mixture $\text{SF}_6 + \text{H}_2 + \text{O}_2$

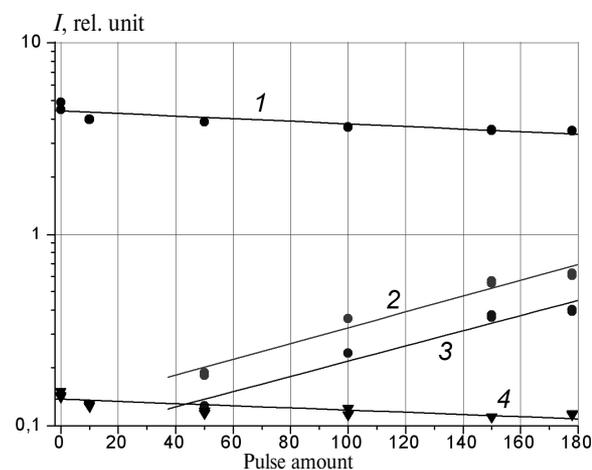


Fig. 4. Dependence of line intensity on pulse number of electron beam: 1) sulfur hexafluoride ($m/z=127$), 2, 3) sulfur difluoride-oxygen ($m/z=86$ and 67), 4) H_2^+ ($m/z=2$)

Original gas mixture (in millimole): $62\text{SF}_6 + 62\text{H}_2 + 10\text{Ar} + 2\text{O}_2$. Argon ($m/z=40$) was introduced for normalizing recorded mass-spectrograms. The main lines typical for gas mixture in the reactor after the influence of electron beam correspond to $m/z=2, 67, 86$ and 127 . The change of line intensity at increasing absorbed dose of pulse electron beam is shown in Fig. 4.

Model mass-spectra of SF_6 and SOF_2 are given in Fig. 5 (electronic library NIST).

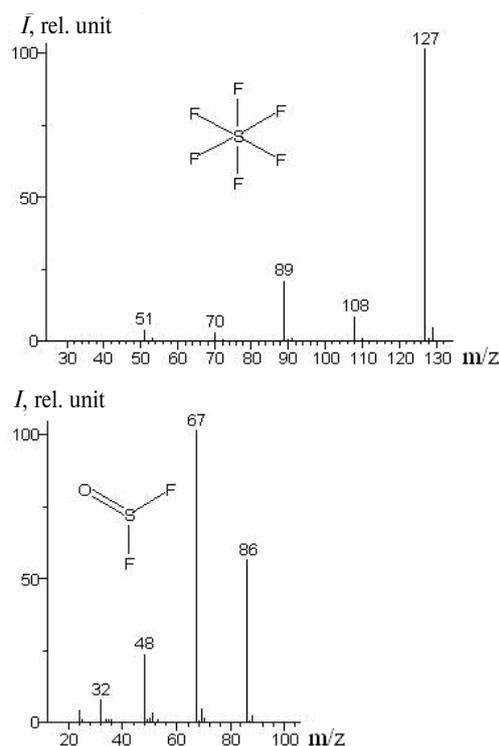


Fig. 5. Model mass-spectra of: a) sulfur hexafluoride and b) sulfur difluoride-oxide

The carried out investigations showed that sulfur difluoride-oxide is the main gas-phase sulfur compound synthesized at conversion of sulfur hexafluoride (in the mixture with oxygen and hydrogen) in low-temperature plasma.

4. Measuring isotope composition of gas-phase compounds

Resolution of MX-7403 was not enough for analyzing isotope composition of sulfur-containing compounds therefore, further mass-spectrometer measurements of sulfur hexafluoride and products of its conversion were carried out by chromatograph-mass-spectrometer TRACE DSQ.

To determine the accuracy of measuring isotope composition of gas-phase compounds by TRACE DSQ mass-spectrum of the original sulfur hexafluoride was analyzed (Fig. 6).

Chromatogram of products of sulfur hexafluoride conversion in the mixture with oxygen and hydrogen contained two peaks. Lines of mass-spectrum of synthesized sulfur difluoride-oxide are also presented in Fig. 6. The degree of conversion of SF_6 did not exceed some percents in the given series of the experiments. Mass-spectrum line intensities of sulfur hexafluoride (SF_5)⁺ and its fission ions (SF_4)⁺, (SF_3)⁺ and (SF_2)⁺, containing isotopes ^{32}S and ^{34}S as well as sulfur difluoride-oxide (SF_2O)⁺ and its fission ion (SFO)⁺, containing isotopes ^{32}S and ^{34}S are given in the Table.

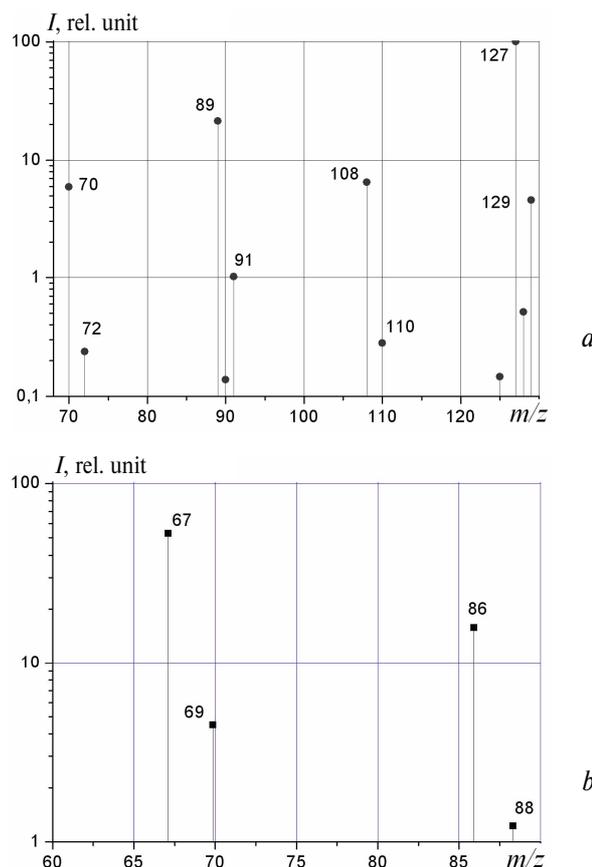


Fig. 6. Mass-spectrum of: a) original sulfur hexafluoride and b) sulfur difluoride-oxide synthesized in plasma of pulse electron beam

Table. Mass-spectrum line intensities of sulfur-containing compounds that is isotope content, %

| m/z | $^{32}\text{SF}_6$ ($^{34}\text{SF}_6$) | | | | $^{32}\text{SOF}_2$ ($^{34}\text{SOF}_2$) | |
|---------------------------------|-------------------------------------------|--------|----------|----------|---------------------------------------------|--------|
| | 70(72) | 89(91) | 108(110) | 127(129) | 67(69) | 86(88) |
| $I_{^{32}\text{S}}$ | 5,95 | 21,4 | 6,48 | 100 | 52,7 | 15,8 |
| $I_{^{34}\text{S}}$ | 0,238 | 1,02 | 0,282 | 4,6 | 4,5 | 1,23 |
| Isotope content ^{34}S | 3,9 | 4,5 | 4,2 | 4,4 | 7,9 | 7,2 |

Conclusion

It was shown that at sulfur hexafluoride conversion in plasma of pulse electron beam the isotope effect is implemented. ^{34}S content in reaction products exceeds datum value in 1,8 times that is significantly higher than measurement error. Thermodynamic modeling of sulfur hexafluoride conversion describes satisfactorily the composition of final decomposition products of SF_6 in plasma of pulse electron beam.

Authors thank research workers of TPU SAC for the help in measuring and analyzing mass-spectra of studied compounds.

The work is fulfilled at the support of RFBR, grant 06-08-00147.

REFERENCES

1. Gorshunov N.M., Gudenko S.V. On possibility of isotope separation owing to nonequilibrium vibrational exchange in afterdischarge zone // Physicochemical processes at atom and molecule selection: Collected reports of the 8th All-Russian scientific conference. – Moscow: CRI atominform, 2003. – P. 133–136.
2. Tumanov Yu.N. Low-temperature plasma and high frequency electromagnetic fields in processes of obtaining materials for nuclear power engineering. – Moscow: Energoatomizdat, 1989. – 279 p.
3. Pushkarev A.I., Novoselov Yu.N., Remnev G.E. Chain processes in low-temperature plasma. – Novosibirsk: Nauka, 2006. – 226 p.
4. Vlasov V.A., Pushkarev A.I., Remnev G.E., Sosnovsky S.A., Ezhov V.V., Guzeeva T.I. Experimental investigation and mathematical modeling of fluoride compound reduction by pulse electron beam // Bulletin of the Tomsk Polytechnic University. – 2004. – V. 307. – № 5. – P. 89–93.
5. Remnev G.E., Furman E.G., Pushkarev A.I., Karpuzov S.B., Kondratiev N.A., Goncharov D.V. Pulse high-current accelerator with matching transformer // Pribory i Tekhnika Eksperimenta. – 2004. – № 3. – P. 130–134.
6. Trusov B.G. Software TERRA for computing plasmachemical processes // Materials of 3^d International symposium on theoretical and applied plasma chemistry. – Ples, 2002. – P. 217–218.

Received on 07.12.2006

UDC 621.039.337

MAGNESIUM ISOTOPES SELECTION AT RECRYSTALLIZATION OF $MgCl_2 \cdot 6H_2O$

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The change of Mg isotope composition at grain-refined zone of $MgCl_2 \cdot 6H_2O$ has been studied. It is shown that light isotope ^{24}Mg enrichment occurs on that crystal end to which grain-refined zone is moving. Isotopes ^{25}Mg , ^{26}Mg are concentrated in the initial crystallization zone. Segregation coefficient increases at influence of constant magnetic field or direct electric current on molten zone. The obtained data are compared with the data on magnesium isotope segregation by the other physicochemical methods.

Introduction

Floating-zone refining often called zone melting is applied for deep purification of substances and their obtaining in single crystal form. As floating-zone refining may be used for separating substances with very close properties and isotopes with low content may be considered with a certain approximation extent as a peculiar impurity to the main isotope then there is a possibility to change the ratio of stable isotopes in salts and metals under the influence of floating-zone refining [1].

Magnesium chloride ($MgCl_2 \cdot 6H_2O$) was chosen as the main object of investigation. Such choice is stipulated by three factors. Firstly, $MgCl_2 \cdot 6H_2O$ is melted at low temperature (116,7°C) that simplifies considerably instrumental process registration; secondly, $MgCl_2 \cdot 6H_2O$ in the experimental conditions is melted completely without the given phase; thirdly, magnesium has three isotopes ^{24}Mg , ^{25}Mg and ^{26}Mg in the ratio 78,60, 10,11 and 11,29 % [2] and in this case ^{24}Mg may be considered as the main isotope and isotopes ^{25}Mg and ^{26}Mg as impurity to the main isotope.

The aim of the work was to study magnesium isotope segregation in the process of floating-zone refining of $MgCl_2 \cdot 6H_2O$ and reveal of factors intensifying this process.

Technique of carrying out the experiments

Investigations were carried out at the samples of $MgCl_2 \cdot 6H_2O$ of «analytically pure» qualification with the length of 100 mm and diameter 3 mm. The samples

were prepared in the following way. Magnesium chloride crystalline hydrate $MgCl_2 \cdot 6H_2O$ was heated to its complete melting and glass tube was filled up with it; after that the tube was soldered from both ends.

Studying the influence of continuous current on change of isotope composition of $MgCl_2 \cdot 6H_2O$ in the process of floating-zone refining the ends of samples were connected by platinum electric contacts with constant current source TEC-42 (HTP 15.10). Voltage equal to 50 V causing continuous current with the strength of 1,3 A in electric circuit was supplied to electrodes. Electric current density amounted to 0,65 A/cm². Motion of melted zone along the sample was performed by sample traveling through stationary heaters.

The experiments were carried out at the device having five zones of heating and cooling. Nichrome wire was used as heating elements. The temperature of molten zone was supported in the range of 120±1 °C that promoted salt area melting by ingot height in 3...4 mm. Melt cooling was naturally-aerial. Temperature of cooling zone amounted to 20±2 °C.

Studying the influence of magnetic field on changing $MgCl_2 \cdot 6H_2O$ isotope composition in the process of floating-zone refining the permanent magnets with magnetic field intensity of 0,3 T were used. Magnetic field intensity was measured by Hall device.

After the experiment 10 mm of each end of glass tube was cut, samples of $MgCl_2 \cdot 6H_2O$ were taken off and analyzed. Preliminary researches showed that at float-