

APPLICATION OF RF (13.56 MHZ) ARC DISCHARGE FOR PLASMA CHEMICAL CONVERSION OF VOLATILE FLUORIDES

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Abstract. The report discusses the use of a new type of plasma source of hydrogen plasma based on a RF (13.56 MHz) arc discharge of atmospheric pressure between two electrodes. This discharge was used for hydrogen reduction of the tetrafluorides of silicon, boron and molybdenum. As a result of the studies, the main regularities of the hydrogen reduction process were established and the main synthesized products were determined. Samples of carbides of silicon, boron and molybdenum were prepared.

Keywords: RF arc discharge, boron fluoride, silicon fluoride, molybdenum fluoride.

1. Introduction

Volatile fluorides of boron ($^{\text{nat}}\text{BF}_3$), silicon ($^{\text{nat}}\text{SiF}_4$) and molybdenum ($^{\text{nat}}\text{MoF}_6$) are the most suitable for the physico-chemical characteristics of the starting materials for preparing their isotopic varieties ($^{10/11}\text{BF}_3$, $^{28/29/30}\text{SiF}_4$, $^{92/94/95/96/97/98/100}\text{MoF}_6$) by the centrifugal method [1]. In the future, already isotopically enriched fluorides can be used to prepare isotopic varieties of B, Si and Mo. The listed isotopes and materials on their basis find application in fundamental scientific research, and also have considerable practical significance. Among the seven stable isotopes of molybdenum, the most important isotopes are ^{98}Mo and ^{100}Mo . Both are used to generate radioactive ^{99}Mo , which turns into $^{99\text{m}}\text{Tc}$, used as a radiopharmaceutical, and the ^{100}Mo isotope can be used in nuclear physics experiments to study double neutrinoless beta decay [2]. It was proposed in [3] to use as starting material molybdenum carbide of a natural composition having a developed surface, which would allow the formed ^{99}Mo atoms to be accumulated with a higher efficiency in comparison with the metal. ^{10}B is mainly used in the control rods of thermal neutron reactors. In order to reduce the size of the control rods while increasing their absorbing capacity with respect to neutrons, the most expedient is the use of highly concentrated ^{10}B in the form of metal ceramic of boron carbide with aluminum oxide [4]. The highly enriched ^{29}Si silicon isotopes in ^{28}Si could be used to develop a quantum computer [5]. An important property of monoisotopic silicon, distinguishing it from a natural analogue, is a higher thermal conductivity which can be used to create various electronic devices [6]. For example, it is known that SiC compound is used to create semiconductor devices of power electronics, and in [7] it is noted that the use of ^{28}SiC significantly improves their performance characteristics. As it has been already mentioned, it is expedient to use their flu-

orides for preparation of the above-mentioned isotopes and materials. The high cost of enriched fluorides requires minimization of return and non-return losses of the substance at the processing stage. Therefore, the development of highly efficient methods for the isolation of isotopically modified silicon, boron and molybdenum from their fluorides is an urgent task. Plasma chemical methods, in comparison with conventional chemical methods, are most preferable for isolation of simple substances and synthesis of compounds from their thermodynamically stable volatile fluorides. The processes of hydrogen reduction of the fluorides of silicon and molybdenum to elementary Si and Mo in the plasma of RF-IC, RFC discharge and RFAD were studied in [8, 9]. The purpose of this work is to study the processes of plasma chemical synthesis of SiC, B_4C and Mo_3C_2 carbides from volatile fluorides of silicon, boron, molybdenum and methane in RFAD discharge at a pressure close to atmospheric and to study the structure of the prepared samples.

2. Description of the discharge

In our case, the discharge is formed between tungsten electrodes in a hydrogen atmosphere in the pressure range 200–760 Torr and represents an electric arc of alternating current with a frequency of $\omega = 13.56$ MHz (Fig. 1a). In this case, there is a strong heating of the end parts of the electrodes that come into contact with the plasma. The electric current in the gas under given conditions is determined by the characteristics of the external circuit. To determine the total current, two electric shunts of alternating current ($r_1 = 2500 \mu\Omega$, $r_2 = 3750 \mu\Omega$) were connected in series to the grounded electrical high-frequency circuit (Fig. 1c). The characteristic value of the total current determined by this technique was $I \sim 5$ A. An estimate of the current was also carried out by estimating the current density of thermoionic emission, knowing

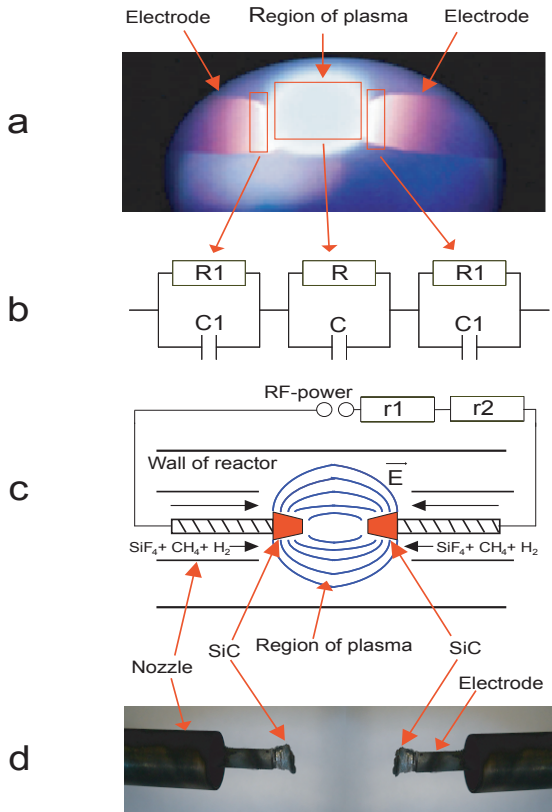


Figure 1. *a* - is a type of discharge; *b* - is the equivalent electrical circuit; *c* - is the scheme of plasma-chemical reactor; *d* - is the type of precipitated B_4C .

the temperature of the electrodes. The temperature was determined by modeling the thermal processes in the reactor [10] and for the selected experimental conditions was equal to 3500 K. For the electrode material used (tungsten) and the known area of the heated surface, the current density is determined by the formula:

$$j = A \cdot T^2 \cdot \exp(-e\varphi/kT) \quad (1)$$

where A for tungsten lies in the interval 40–100, $e\varphi = 4.54$ eV [11]. Knowing the area of the heated electrode surface, the estimated current value is $I \sim 5$ A. It can be seen that the experimentally obtained value of the total current coincide with the current value estimated by 1. A double electric layer (DEL) model was used to describe the RF discharge under consideration. Formation of DEL occurs in the area of contact of the metal surface of the electrodes and plasma [11]. According to the adopted model, the equivalent circuit of our discharge is the circuit shown in Fig. 1b. R is the active resistance of the plasma, $C = \epsilon S/(4\pi L)$ is the capacity of the space between the DEL filled with plasma, where S is the characteristic cross-sectional area of the plasma arc, L is the characteristic dimension of the plasma, $\epsilon = -\omega_{pe}^2/\nu_{en}^2$ is the dielectric constant of the plasma), $R1$ is the active resistance resulting in the heating of the electrodes, connected

with the flow of thermoelectrons and electrons that have passed from the plasma through the DEL to the electrodes, $C1 = S1/(4\pi d)$ is the capacity of the DEL, where $S1$ is the area of the electrodes, $d = 3r_D$ (the radius of the Debye) is the characteristic longitudinal size of DEL. The value of R is determined by the formula $R = L/\sigma S$, where L is the characteristic dimension of the plasma, S is the characteristic cross-sectional area of the plasma arc, and $\sigma = \omega_{pe}^2/4\pi\nu_{en}$ is the conductivity of the plasma [12]. The resistance and impedances of this circuit are calculated according to this formula and are equal to $R = 6 \Omega$, $Z_C = 10 \Omega$, $Z_{C1} = 400 \Omega$, where $Z_C = 1/i\omega C$ is the impedance capacitance C . Since R is comparable with Z_C , there are two components of the electric current in the plasma: the conduction current and the bias current. The value of $R1$ due to the current of thermoionic emission can not be calculated, but judging by the strong heating of the electrodes, $R1 < Z_{C1}$ and the current in the region of DEL is the conduction current, which in our case is 5 A. The role of the bias current is reduced to the transfer of energy through the discharge gap without absorption. Thus, the major part of the energy is released in the near-electrode region, where the deposition of the target product takes place and energy consumption is less as compared with the arc discharge.

3. Experimental

This type of discharge was used to study the processes of hydrogen reduction of fluorides of silicon, boron and molybdenum and synthesis of their carbides at a total reactor pressure of 240 and 760 Torr. Hydrogen was used as the plasma-forming gas. The molar ratio of $H_2/SiF_4/CH_4$ and $H_2/BF_3/CH_4$ was maintained at 9/1.5/1 and the molar ratio of $H_2/MoF_6/CH_4$ equal to 45/1.5/1. The plasma-chemical reactor was a silica glass tube, inside which the rod electrodes were placed equipped with gas flow generators and connected to RF generator (Fig. 1c). During the synthesis of SiC and B_4C , deposition was carried out at the ends of the electrodes in contact with the plasma (Fig. 1d), and in the synthesis of Mo_3C_2 , its finely dispersed fraction precipitated on a porous nickel filter. The process of conversion of the fluorides of silicon, boron and molybdenum into their carbides and other possible by-products of the reaction was studied experimentally. The total conversion of fluorides and the presence of gas phase reaction products were determined by IR spectroscopy. The samples were analyzed by X-ray phase analysis, electron microscopy, laser mass spectroscopy, and laser diffraction.

4. Results and Discussion

During the research, in the synthesis of silicon carbide, in gas-phase products at the outlet of the plasma chemical reactor, $SiHF_3$, CF_4 , C_2H_4 , C_2H_2 and CO_2 were detected. In the synthesis of boron carbide, C_2H_4 ,

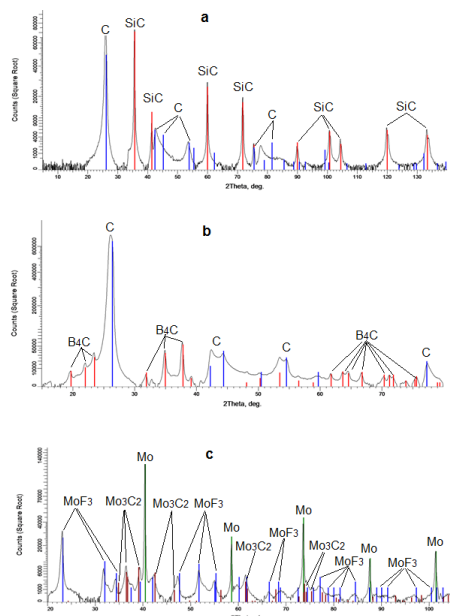
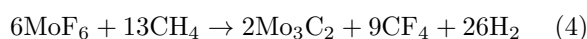
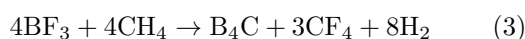
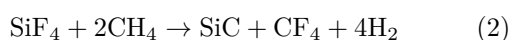


Figure 2. X-ray phase analysis of the samples of silicon carbide (a), boron carbide (b) and molybdenum carbide (c).

C₂H₂ and CO₂ were also found in the gas phase. In addition, an oily liquid condensed on the walls of the plasma chemical reactor, which represented the complex [CH₃BF]⁻H⁺. It should be noted that both during the synthesis of silicon carbide and the synthesis of boron carbide, the hydrogen fluoride (HF) was not observed in gas phase products. The intensive growth of silicon carbide and boron carbide was observed on electrodes in the form of cylindrical polycrystal, and finely dispersed soot precipitates on the walls of the plasma chemical reactor. According to X-ray phase analysis (Fig. 2a,b), samples of silicon carbides and boron contain up to 40% of carbon. In the process of synthesis of molybdenum carbide in the exhaust gas mixture, due to small concentration of methane in the initial mixture entering the plasma chemical reactor, the ethylene and acetylene were not observed. The formation of solid-phase products, which include molybdenum carbide, molybdenum and MoF₃, is observed in the volume of the plasma chemical reactor in the form of intense dust formation (Fig. 2c). On the basis of the experimental data obtained, it is possible to assume the basic chemical reactions responsible for the formation of carbides of silicon, boron and molybdenum:



According to morphological studies, Mo₃C₂ is formed as a nano-powder with a particle size of 50–70 nm

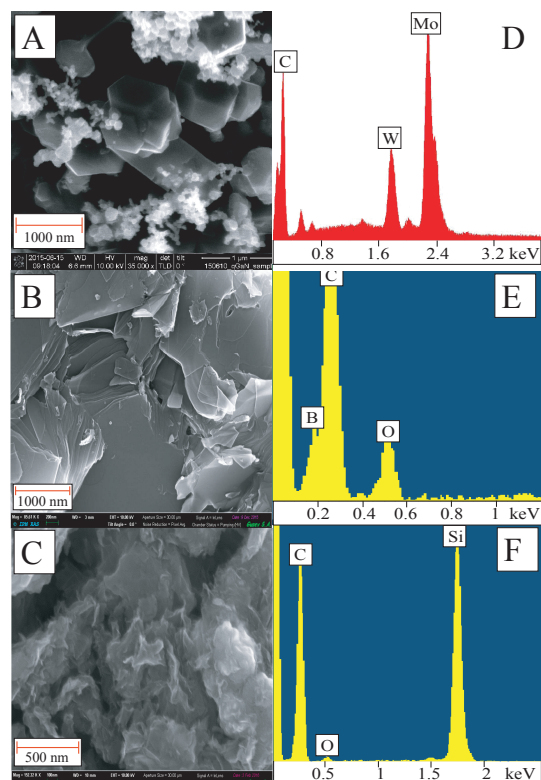


Figure 3. A - Morphology of samples Mo₃C₂, B - B₄C, C - SiC, and their element composition (D), (E) and (F), respectively.

(Fig. 3a). Samples of boron carbide and silicon have a layered structure (Fig. 3b,c). It is possible to say with a high degree of probability that the growth of B₄C and SiC occurs layer by layer. A prerequisite for growth is the initial deposition of a graphite layer on the electrode surface. Graphite precipitates on the surface of the electrode heated up to 3000–3500 K as a result of pyrolysis of methane, forming dendrites. The electric field strength and its gradient on the generated dendrites are high, which allows the SiF₄ or BF₃ molecule to be polarized, and the Si or B layer is deposited. Then, graphite precipitation is required again. The samples grown under these conditions should contain a significant amount of free carbon, which is confirmed by X-ray analysis data.

5. Conclusions

As a result of these studies, the main gas-phase and solid-phase products in the synthesis of the carbides of silicon, boron and molybdenum were determined. The main chemical reactions responsible for the formation of target products – carbides – are proposed. The assumptions are proposed for the mechanism of growth of polycrystalline carbides of silicon and boron on the surface of the electrodes. Samples of carbides of silicon, boron and molybdenum were prepared and

their phase, elemental and impurity composition were studied.

Acknowledgements

This work was financially supported by Russian Scientific Foundation Grant 17-13-01027.

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