Phase composition of powder products obtained in direct current atmosphere arc plasma synthesis at the “molybdenum-carbon” system

A Ya Pak, Y Tu Yakich and O V Tarasova
National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk, 634050, Russia
E-mail: ayapak@tpu.ru

Abstract. In this paper you can see the results of experimental studies that are devoted to the production of powder. To obtain these materials, an electric arc method without vacuum was used, based on the effect of spontaneous shielding of the reaction zone by gaseous products of combustion of a direct current arc discharge in the gap between graphite electrodes. A feature of the approach used is its implementation without the use of vacuum equipment. The process of electric arc synthesis is implemented in a cylindrical cavity of a graphite cathode, in which a powder mixture of carbon and molybdenum is present. As a result of experiments, multiphase powder products were obtained, which were collected from various parts of the discharge loop electrode system. Three types of products were obtained: collected from the walls of the cylindrical cavity of a graphite cathode, collected from its bottom, and also collected in the form of a cathode deposit. Differences in the phase composition of the products obtained were revealed, and the morphology of micro-sized particles in the synthesis product was determined.

1. Introduction
Molybdenum carbide is a well-known catalyst for hydrogen production reactions that can potentially replace a number of platinum-group metals in expensive catalysts [1–2]. Molybdenum carbide is obtained in several techniques. In general, three groups of methods can be distinguished. The first group of methods is based on heating molybdenum or its oxide with atomic carbon in vacuum, hydrogen or, less commonly, hydrocarbon gases at temperatures of 1200 to 2000°C. To this group the methods implemented in the furnaces of different principles of action, the method of self-propagating high-temperature synthesis, other methods that allow you to get bulk specs containing molybdenum carbide can be attributed. To the second group of methods can be attributed approaches aimed at obtaining thin films, including magnetron sputtering of initial reagents, the method of chemical vapor deposition, electrochemical methods. It is customary to refer to the third group methods that are implemented by the interaction of molybdenum, its oxide or salt with a carbonizing agent, which can be carbon-containing gas or usually powdered carbon, which results in a powder product with a high specific surface [3]. There are widely known works in the world that are devoted to the preparation of various crystalline phases of molybdenum carbide and the determination of catalytic activity as catalysts for hydrogen evolution reactions, for example[4–5].

One of the approaches to the preparation of molybdenum carbide is electric arc [8]. In recent years, a type of electric arc technique has been actively developed, which is implemented in the direct
current (DC) arc discharge plasma initiated in ambient air [9]. This method is used to obtain carbon nanostructures, for example, nanotubes [4–7]. The method is implemented by generating gaseous carbon monoxide, which shields the working volume from atmospheric oxygen, which makes it possible to dispense with a sealed reactor vessel, vacuum equipment and significantly improve the technical and economic performance of a plasma reactor [9–12]. This method was previously used by our scientific group to obtain silicon carbide [13]. This paper presents the results of experimental studies on the study of powder materials obtained in the DC arc discharge plasma initiated in an ambient air conditions.

2. Experiment
A series of experiments was carried out on a DC electric arc reactor. The reactor contains a graphite anode and a cathode connected to a direct current source. A DC source with pulse-width modulation is able to regulate the operating current of the discharge circuit. The cathode is made in the form of a graphite crucible, in the cylindrical cavity of which an arc discharge is ignited. The anode is made in the form of a solid graphite cylindrical rod. The length of the discharge gap is set at the initial time of 0.5±0.1 mm using a linear electric drive based on a stepper motor. In the combustion zone, a powder mixture of molybdenum and carbon was preliminarily added in a quantity of Mo:C = 3:1 in an amount of 0.50±0.05 g. The experiment was performed three times for 10.5±0.3 seconds. After a predetermined time has elapsed, the power supply to the installation was terminated. As a result of the experiment to obtain a powdered product, three different ways are collected: 1) the powder was collected from the side walls of the cylindrical cavity inside the cathode (type 1 sample); 2) the sample was collected in the cavity of the cylindrical crucible-cathode in the area of formation of the arc discharge, i.e. a cathode deposit was collected, which was ground into powder using an agate mortar (type 2 sample); 3) the powder was collected from the annular surface around the cathode deposit (type 3 sample).

The obtained powder materials were analyzed by X-ray diffraction (ShimadzuXRD7000, CuK\(_\alpha\)), scanning electron microscopy (TescanVega 3 SBU with an Oxford X-Max-50 energy dispersive analyzer).

X-ray phase analysis is of high quality and is carried out using the PDF4+ structural data base.

3. Results and discussion
During the arc discharge process, the actual measured current was about 150 A at a discharge voltage of about 30 V. Significant interference with the recorded electrical signals is a known difficulty in monitoring the operating modes of electric arc reactors, and seems to be the norm [14]. Nevertheless, the oscillograms of the operating mode determined the electric power of the arc discharge, as well as the amount of released energy. According to the data obtained, 45.1 kJ of energy was released in the system; accordingly, the average discharge power was about 4.3 kW. Thus, the energy consumption of the process can be roughly estimated as 90.2 kJ g\(^{-1}\), and the system performance is 0.05 g s\(^{-1}\).

Typical X-ray diffraction patterns of the above three types of synthesis products are presented in figure 1.

According to the data presented above, the separate collection of the product of synthesis in the system under consideration allows one to isolate material with different phase composition. In particular, it is possible to distinguish a product with zero content of the original molybdenum. In addition, the effect on the ratio of synthesized phases Mo\(_{1.2}\)C\(_{0.8}\) and Mo\(_2\)C is possible: the Mo\(_{1.2}\)C\(_{0.8}\) phase is mostly formed in the deposition zone of the cathode deposit. According to the known data [15], in the reaction zone the temperature field is strongly non-uniform, the temperature can vary from 10000 to 3000–5000 K with a distance of only a few millimeters from the surface of the arc discharge forming on the electrode surface. In addition, in the zone of formation of the cathode deposit is significantly higher concentration of carbon atoms. This can explain the significant differences in the phase composition of the products of synthesis, as well as the formation of two crystalline phases of molybdenum carbide.
Figure 1. Typical X-ray diffraction patterns. 1. Product type 1 (from the side walls of the cathode). 2. Product type 2 (cathode deposit). 3. Product type 3 (from the surface around the cathode deposit).

According to the scanning electron microscopy (SEM) there are 3 main object types in the synthesized samples (figure 2). The first type is the low density mass, which is considered to be graphite particles agglomeration. Energy dispersive analysis (EDX) confirms that carbon is the main part of the elemental content of these particles. It is possible to see the density difference in the phase contrast mode. The second type of particle is represented by more dense crystals 1–3 μm in size. These particles are identified as initial raw molybdenum because of its elemental content and size which are respect to initial molybdenum particles. The third type of particles is molybdenum and carbon contained crystals less than 1 μm in size. These particles are identified as molybdenum carbide phases. In this stage of research unfortunately it was not possible to see the difference in two molybdenum carbide phases morphology. In general according to the EDX analysis powder samples contain molybdenum (up to 60% mass), carbon (up to 30% mass), some oxygen (up to 5%) and some impurities such as Fe, S, Al, etc. (up to 5%).

Figure 2. SEM pictures of the synthesized powder samples in phase contrastmode (a) and standard mode (b)
4. Conclusion
As a result of summarized studies, products with different phase composition were obtained. All the products obtained contain two phases of molybdenum carbide $\text{Mo}_{1.2}\text{C}_{0.8}$ and $\text{Mo}_2\text{C}$, the formation of which at the same time can be explained by a significant temperature gradient and carbon concentration in the reaction zone. It should be noted that the products obtained were synthesized by a vacuum-free electric arc method.

Acknowledgements
The work was performed within the framework of the Grant of the President of the Russian Federation for state support of young Russian scientists (candidates of science), project number MK-633.2019.8.

References
[1] Lin L et al 2017 Nature 544 80
[2] Maa Y, Guana G, Hao X et al 2017 Renewable and Sustainable Energy Reviews 75 1101
[3] Baklanova O N et al 2017 Journal of Alloys and Compounds 698 1018
[4] Dantas S L A, Lopes-Moriyama A L, Sena M S et al 2018 Ceramics International 44 20551
[5] Vitalea G, Guzmán H, Frauwallner M L et al 2015 Catalysis Today 250 123
[6] Yang X, Feng X, Tan H et al 2016 Journal of Materials Chemistry A 4 3947
[7] Huang Y, Wang C, Song H et al 2018 International Journal of Hydrogen Energy 43 12610
[8] Saito Y, Matsumoto T and Nishikubo K 1997 Journal of Crystal Growth 172 163
[9] Arora N and Sharma N N 2014 Diamond and Related Materials 50 135
[10] Su Y, Wei H, Li T, Geng H and Zhang Y 2014 Materials Research Bulletin 50 23
[11] Su Y, Zhou P, Zhao J, Yang Z and Zhang Y 2013 Materials Research Bulletin 48 3232
[12] Zhao J, Su Y, Yang Z, Wei L, Wang Y and Zhang Y 2013 Carbon 58 92
[13] Pak A Ya and Mamontov G Ya 2018 Technical Physics Letters 44 615
[14] Yeh Y-W, Raitses Y and Yao N 2016 Carbon 105 490
[15] Schur D V et al 2007 Carbon 45 1322