Morphology features of molybdenum carbide synthesized by DC arc discharge plasma in air

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Abstract. This paper presents the XRD and SEM analysis results of molybdenum carbide powder synthesized by DC arc discharge plasma in air. The regularities of the phase composition distribution in the reaction zone are revealed. It was determined that in the arcing zone the initial molybdenum is completely processed, the hexagonal molybdenum carbide has the greatest yield. As a distance from the arcing zone increases, the fraction of cubic molybdenum increases, orthorhombic molybdenum carbide and graphite phases decreases. According to SEM data, the features of element composition and morphological types of samples collected from different parts of the reaction zone were revealed.

1. Introduction
Molybdenum carbides have excellent physical and chemical properties such as high hardness and wear resistance, high melting point, good heat resistance, relatively high electrical and thermal conductivity. They are widely used in mechanical engineering as components of hard alloys for the manufacture of cutting tools, in electrochemistry as electrocatalysts and counter electrodes for solar cells, as well as in supercapasitors, biosensors, etc. [1-6].

The main methods for molybdenum carbides synthesis are laser ablation [7], CVD [8], and SPS [9]. In recent years, non-vacuum arc discharge methods have been widely used. Such method has a lot of advantages, main of them are simplifying the system design and increasing the energy efficiency of synthesis [10]. The possibility of obtaining molybdenum carbide by DC arc discharge plasma in ambient air was showed earlier in [11]. This work is focused on identifying the features of chemical composition and morphological types of samples collected from different parts of the reaction zone.

2. Experimental part
The experiments were carried out using a laboratory DC arc discharge reactor, the scheme of which and the principle of its operation are described earlier in [11]. A mixture of microsize molybdenum with an average particle size of 1-5 μm and graphite were used as initial reagents in a mass ratio of Mo:C = 3:1 in an amount of 0.5 g. The synthesis parameters are current strength of the power source of 165 A and the amount of released energy of ~ 45 kJ. The time of arcing was the same for all experiments and equal to ~ 10 s. After that, the product was collected from different parts of the reaction zone: from the crucible bottom directly in the cathode spot (type A), from the crucible bottom outside the cathode spot (type B) and from the inner surface of crucible walls (type C).
The synthesized product was analyzed by X-ray diffractometry (XRD, Shimadzu XRD-7000, Cu-Kα radiation) and scanning electron microscopy (SEM, Tescan Vega 3 SBU with an Oxford X-Max-50 energy dispersive analyzer).

3. Results and discussion

Figure 1 shows a typical XRD pattern of the synthesized product and the dependence of the relative intensities of the main maxima on the samples type (A, B, C). As it can be seen, in type A samples the main crystalline phase is graphite (C), also there are orthorhombic (Mo₂C) and hexagonal (Mo₁₂C₀·₈) molybdenum carbide phases. Unlike other types, there is no cubic molybdenum phase (Mo) in the composition of this type. The following phases can be identified in type B samples: C, Mo, Mo₂C and Mo₁₂C₀·₈. Also in this type samples, the intensity of the orthorhombic molybdenum carbide main diffraction maxima is almost equal to the relative intensity of the graphite main diffraction maxima. In type C samples, the main crystalline phase is cubic molybdenum. There is also a graphite phase and phases of molybdenum carbides Mo₂C and Mo₁₂C₀·₈, as well the intensity of the Mo₂C main maxima is higher than the relative intensity of the graphite one.

![Figure 1](image)

The differences in phase compositions can be explained by the energy and temperature distribution. Type A samples were obtained in the cathode spot zone, i.e. in the region of the highest temperatures from the considered ones and the highest concentration of carbon atoms due to their transfer from the anode to the cathode during the arcing. For these reasons, samples of this type are characterized by a phase composition in which the initial molybdenum is completely processed to carbides and the graphite phase dominates. Type B samples were obtained at a lower temperature range (~ 2000 –3000 K) and outside the zone of increased carbon atoms concentration. Therefore, type B samples contain a significant amount of the cubic molybdenum phase. In type C samples collected from the cathode walls, as in products obtained at the greatest distance from the arcing zone, and apparently located at lower temperatures, the main phase is cubic molybdenum.

According to the SEM data combined with energy dispersive analysis (Fig. 2), the main microdimensional morphological types were identified in the synthesized products (Table 1). In samples of all types, there is a carbon matrix (1), particles containing molybdenum carbides (2) and clusters with molybdenum carbides particles (3). A particles not previously identified are clusters (4) containing iron. This type of particles was found only in samples collected from the cathode walls. Probably, plasma interacts with anode current-carrying metal holders located directly above the cathode during the arcing. As a result, iron compounds can be detected in the upper region of the cathode walls. Also, previously there were no detected particles (5), consisting almost entirely of molybdenum. These are probably
molybdenum particles formed from the melt. They are usually present at the crucible bottom, both in the cathode spot zone and beyond.

According to EDS analysis, the products consist mainly of molybdenum, carbon, oxygen, iron and other chemical elements (aluminum, silicon, calcium, sulfur, etc.). Moreover, the proportion of iron (up to 6 wt.% and oxygen (up to 11 wt.%) is significant in the type C samples. In type B samples, the iron content decreases to 1.7 wt.%, oxygen - to 4.7 wt.%. Type A samples are characterized by an oxygen content of not more than ~ 2 wt.% and an iron content close to zero (within the method error).

![Figure 2. SEM images of type A (a,d), B (b,e) and C (c,f) samples.](image)

**Table 1.** The main microdimensional morphological types in the samples.

| no | Type of particles                          | Features                                                                 | The presence at samples |
|----|-------------------------------------------|----------------------------------------------------------------------------|------------------------|
|    |                                          |                                                                           | Type A | Type B | Type C |
| 1  | Carbon matrix                             | Many images contain submicron and micron molybdenum particles             | +      | +      | +      |
| 2  | Molybdenum carbides particles             | Contain molybdenum carbides Mo$_2$C and Mo$_{1.2}$C$_{0.8}$               | +      | +      | +      |
| 3  | Clusters with molybdenum carbides particles | The size of several μm                                                   | +      | +      | +      |
| 4  | Clusters with iron                        | Formed in the upper region of the cathode                                | -      | -      | +      |
| 5  | Molybdenum particles                      | Melted forms Size ~ 100 μm                                              | -      | +      | +      |
| 6  | Molybdenum particles                      | Melted forms close to spherical Size ~ 100 μm                            | -      | +      | -      |
| 7  | Molybdenum and carbon particles           | Flat smooth edges with signs of chips Size up to ~ 100 microns           | +      | +      | -      |
On the one hand, the presence of oxygen is a norm for all powders due to adsorption. On the other hand, based on XRD data and due to the presence of iron in the type C samples we can conclude about the influence of the external environment on the product in the upper region of the cathode cavity. In this regard, it seems appropriate to collect synthesis products from the cathode bottom and from the lower half of the cathode wall.

4. Conclusion
Thus, in this work, we synthesized molybdenum carbide powder by DC arc discharge plasma in air. Based on the XRD and SEM results, the features of the product collected from different parts of the reaction zone: from the crucible bottom directly in the cathode spot, from the crucible bottom outside the cathode spot and from the inner surface of crucible walls, are revealed. It was found that it is advisable to collect synthesis products from the cathode bottom and from the lower half of the cathode wall.

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