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## Synthesis of micro-sized powders of molybdenum borides by atmospheric AC arc discharge

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The results of experimental studies proving the possibility of synthesis of molybdenum borides crystalline phases by atmospheric AC arc discharge are presented. According to X-ray diffractometry, there are four crystalline phases  $\text{Mo}_2\text{B}$ ,  $\text{MoB}$ ,  $\text{MoB}_2$  and  $\text{Mo}_2\text{B}_5$  in powder products obtained at different atomic ratios of molybdenum and boron. According to scanning electron microscopy data, molybdenum boride particles are characterized by a wide size distribution from  $10\ \mu\text{m}$  to  $100\ \mu\text{m}$  forming agglomerates with sizes up to  $\sim 550\ \mu\text{m}$ .

**Keywords:** molybdenum boride, arc discharge, alternating current, vacuum-free method.

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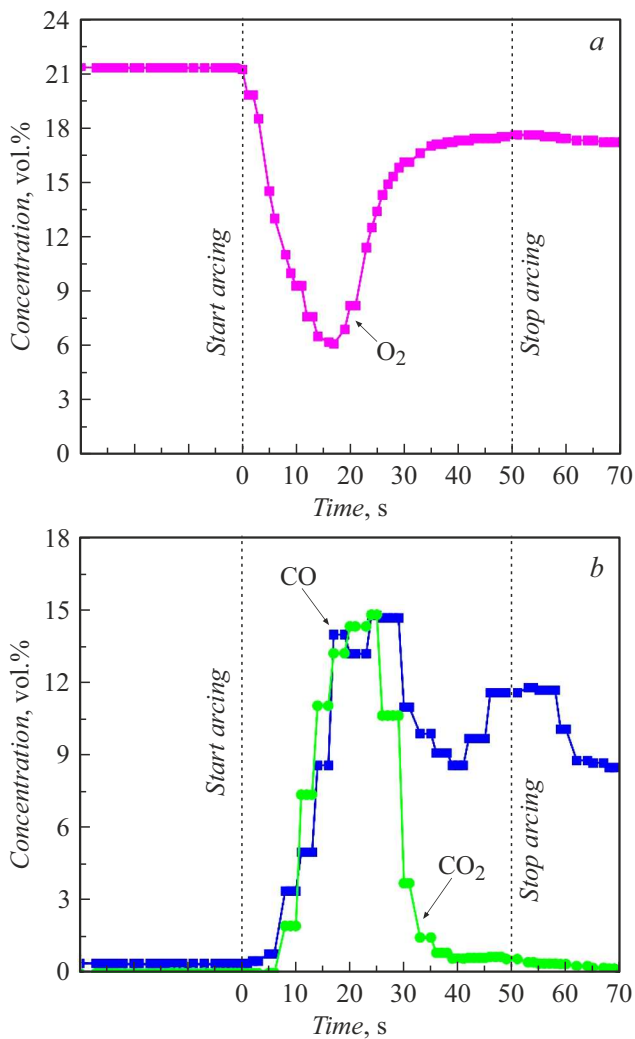
Most metal borides are ultrahard materials that find use in the processing industry. A number of experimentally determined and calculated crystal structures of molybdenum borides with promising physical and mechanical properties are known [1]. In addition, the issues of potential application of molybdenum borides as constituents of various catalysts are being discussed extensively [2,3]. Several methods for synthesis of molybdenum borides are known: mechanical synthesis, self-propagating high-temperature synthesis, volume combustion synthesis, thermobaric method, etc. [4–9]. Electric-arc techniques for synthesis of carbon nanostructures and known and novel carbides have advanced rapidly in recent decades [10–13]. Several crystalline phases of tungsten borides have been synthesized successfully in a well-known process involving the use of a DC arc discharge initiated in an open atmospheric environment with the effect of so-called self-screening of the reaction volume [14]. At the same time, despite the fact that tungsten and molybdenum borides are structural analogs, literature data on the possibility of synthesis of crystalline phases of molybdenum borides by the vacuum-free electric-arc method are lacking. Experimental evidence of feasibility of application of the vacuum-free AC electric-arc method in synthesis of specific carbides, borides, etc., are also lacking.

A series of experiments on synthesis of molybdenum borides were carried out using a proprietary laboratory AC electric-arc setup. The initial mixture of micrometer-sized molybdenum and X-ray amorphous boron was introduced into a graphite crucible with a cover ( $1.000 \pm 0.005\ \text{g}$ ), which was mounted inside a large graphite crucible. This large crucible was connected to one pole of a power supply. A cylindrical graphite rod was connected to the other pole. An AC arc discharge was initiated between the cover of the small graphite crucible and the end of the cylindrical graphite rod and sustained for 50 s. The current power

was set within the  $300 \pm 5\ \text{A}$  range. With such process parameters, the crucible with the charge stock was heated completely to a temperature of  $1517^\circ\text{C}$  (with a standard deviation of  $57^\circ\text{C}$ ) at half its height. This temperature range is sufficient for synthesis of molybdenum borides [15]. At an arc voltage of 36–37 V, the energy supplied was 537 kJ (with a standard deviation of 14 kJ). The atomic ratio of Mo and B was varied within the range from 1/1 to 1/15 in different series of experiments. The composition of the gas medium within a hollow space in the large graphite crucible was determined in the process of each experiment by a Test-1 continuous-flow gas analyzer (Boner, Russia). Powders taken out of the graphite crucible were analyzed after each experiment by X-ray diffraction (Shimadzu XRD7000s, Japan,  $\text{CuK}_\alpha$  radiation) and scanning electron microscopy (Tescan Vega 3 SBU with a chemical composition analyzer, Czech Republic).

Figure 1 illustrates the variation of concentrations of gases within the graphite crucible in the process of AC arcing. It is evident that the oxygen concentration decreases from the level normal for air to approximately 5–6 vol.% (Fig. 1, *a*). At the same time, the concentrations of CO and  $\text{CO}_2$  gases increase to 14–15 vol.% (Fig. 1, *b*). These data are indicative of oxidation of carbon in electrodes and the formation of an autonomous gas environment. It should be noted that atmospheric air is present in the gas circuit of the analyzer and the system is not isolated; therefore, it is likely that the concentration of oxygen is overestimated, while the concentration of CO and  $\text{CO}_2$  gases is underestimated. Thus, self-screening of the reaction volume, which was used earlier in synthesis of tungsten borides [14] by DC arc discharge, was achieved. The effect of self-screening of an AC arc discharge in synthesis of metal borides has been observed experimentally for the first time.

Figure 2 presents the X-ray diffraction patterns for powders in a series with an increasing Mo/B atomic ratio:



**Figure 1.** Results of analysis of the gas medium in the course of processing of a mixture of molybdenum and boron by an atmospheric AC arc discharge.

1/1, 1/5, 1/10, and 1/15. The lack of identifiable maxima indicating the presence of initial molybdenum implies that it was used up in the course of arc processing of the charge stock. Diffraction maxima corresponding to phases of boron oxides and molybdenum oxides also could not be identified, suggesting that self-screening with suppression of oxidation of synthesis products was achieved. Crystalline phases  $\text{Mo}_2\text{B}$ ,  $\text{MoB}$ ,  $\text{MoB}_2$ , and  $\text{Mo}_2\text{B}_5$  were identified. Phases of higher borides  $\text{MoB}_{5-x}$ , which were thought to be likely to form in view of literature data [16] for an Mo/B ratio of 1/10–1/15, were not found. It should also be noted that boron carbide, carbon nitride, and molybdenum nitride phases were not identified (within the sensitivity of X-ray diffractometry) in synthesis products. However, diffraction maxima possibly corresponding to boron nitride (BN) and molybdenum carbide ( $\text{Mo}_2\text{C}$ ) were visible. It is not possible to prove decidedly the presence of carbide, boride, and nitride phases and determine the exact qualitative com-

position in the considered multiphase system that exhibits numerous diffraction maxima complying with the principles of superposition. Thus, the reaction of boride formation is apparently dominant in the studied system. The results of evaluation of the phase composition of synthesis products are broadly consistent with the current understanding of the boron–molybdenum constitution diagram [17].

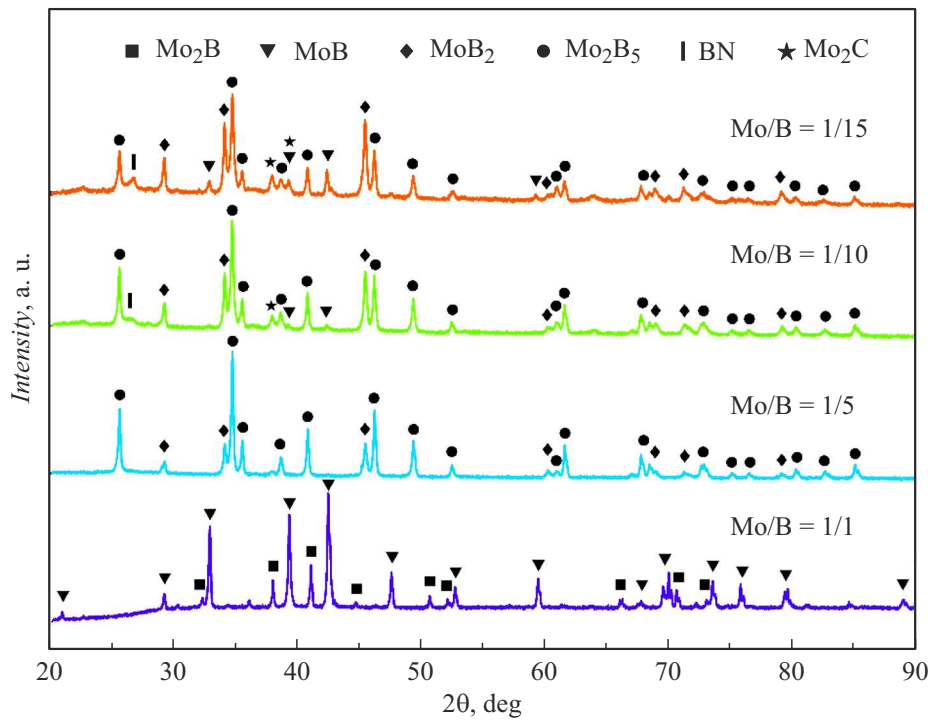
Scanning electron microscopy data (Fig. 3) revealed that a round shape is typical of synthesized particles; both individual particles and their agglomerates were observed. Typical particles of molybdenum borides are 10–100  $\mu\text{m}$  in size and form agglomerates as large as  $\sim 550 \mu\text{m}$ . The maximum of their distribution is located within the interval from 20 to 40  $\mu\text{m}$ . A broad particle size distribution is typical of electric-arc synthesis, since a considerable temperature gradient is established in the synthesis process. According to the results of energy-dispersive analysis of samples from the mentioned series, all of them clearly contain boron (53.55 at.% with a standard deviation of 12.34 at.%) and molybdenum (13.31 at.% with a standard deviation of 7.18 at.%). Localized particles with the maximum boron concentration (85.93 at.% with a standard deviation of 0.52 at.%), which are characterized by a darker contrast in images obtained in the backscattered electron mode (Fig. 3, a), were also found. In addition, local presence of nitrogen (from 7.89 to 26.60 at.%) and carbon (from 15.92 to 30.37 at.%) was identified in samples with the highest boron fraction ( $\text{Mo/B} = 1/10\text{--}1/15$ ). These results may provide indirect proof of the presence of individual carbide and nitride particles in synthesis products. Several impurity chemical elements (namely, oxygen, iron, sulfur, and silicon) with an overall concentration no greater than 2 at.%, which could be components of the charge stock or crucibles and could enter the product in the course of sample synthesis, collection, and transport, were also present.

The presented results of experimental studies allow us to make the following conclusions.

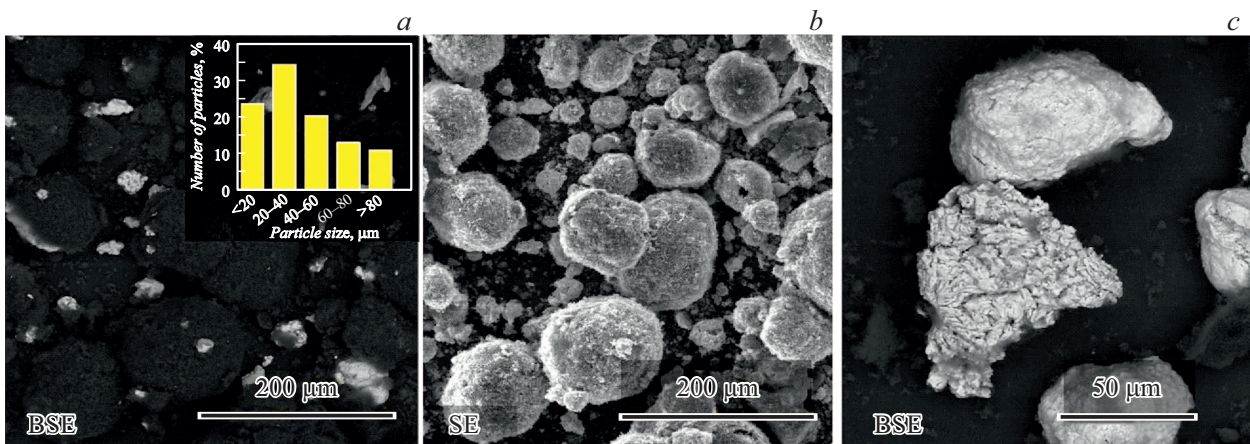
(1) The effect of self-screening of the reaction volume from ambient oxygen, which has earlier been thought feasible only for DC arc discharges, has been observed for the first time in an AC arc discharge. This provides an opportunity to expand significantly the boundaries of so-called vacuum-free electric-arc synthesis and continue the work on refinement of the experimental procedure and equipment.

(2) The proposed experimental design is the simplest of all similar ones, since only the charge stock, graphite electrodes, and an AC source are needed. In general, the vacuum-free electric-arc method has an advantage over similar techniques in the simplicity of its design, an increased energy efficiency, a broad range of attained temperatures, and low requirements as to the charge stock.

(3) The feasibility of synthesis of crystalline phases of molybdenum borides in a Russian-developed vacuum-free AC electric arc discharge process in an open atmospheric environment has been demonstrated for the first time.



**Figure 2.** Typical X-ray diffraction patterns of powdered synthesis products obtained in a series of experiments with the Mo/B atomic ratio in the charge stock varying from 1/1 to 1/15.



**Figure 3.** Typical images of the synthesis product obtained with a scanning electron microscope. *a*, *c* — Backscattered electron (BSE) mode; *b* — secondary electron (SE) mode.

Further studies are planned to be focused on the optimization of energy consumption values, scaling, estimation of the electrode consumption rate, and evaluation of the possibility of synthesis of other metal borides and carbides with the use of the proposed method.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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