Chemistry for Sustainable Development **13** (2005) 197–204

Obtaining the Composite MoB Material by Means of Force SHS Compacting with Preliminary Mechanical Activation of Mo–10 % B Mixture

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Abstract

The reactivity of the mixture Mo–10 % B is investigated, along with the effect of the parameters of mechanical activation on heat evolution, specific surface, structure of powders, activation energy of combustion process, heat evolution rate, temperature and rate of combustion. It is shown that activation in the optimal regimes increases the reactivity of low-exothermal mixture Mo–10 % B. Using the technology of force compaction, a multilayer composite target for magnetron sputtering was obtained. It was established that the density and hardness of the synthesized material increase in the case if preliminary mechanical activation is applied.

INTRODUCTION

One of the methods to increase the performance characteristics of a material is to deposit high-melting coatings. It seems interesting to use molybdenum borides MoB and Mo_2B_5, and their compounds with nitrogen Mo–B–N as the protective coatings.

In order to broaden the areas of application of complex multicomponent coatings deposited by means of ion plasma and magnetron sputtering, it is necessary to develop new composite cathodes. Relatively high chemical activity of Mo and B hinders obtaining chemically pure molybdenum borides because of contamination with the products of side reactions and with admixtures. The self-propagating high-temperature synthesis procedure (SHS) allows one to unite into one stage the synthesis of a high-melting material of the required composition, providing its necessary purity, and preparation of a composite target of magnetron sputtering with high density, strength, homogeneity of the structure, and the necessary dimensions. A low impurity content of the materials obtained using the SHS technology is achieved due to self-purification of the synthesis products in a combustion wave [1].

Carrying out the SHS process in weakly exothermal mixtures, to which the system under investigation Mo–10 % B belongs (with the thermal effect of reaction <1 kJ/mol), one should use definite operations increasing the reactivity of the mixture and ensuring the combustion process to proceed in the steady regime. One of the efficient methods to intensify solid-phase reactions is mechanical activation (MA) of a mixture of solid reagents in high-energy machines (planetary mills) [2–5] due to which favourable conditions are created for the interaction between the components of the mixture. A specific feature of this system is low adiabatic combustion temperature (T_{ad}) which is equal to 2310 K [6]. This is lower than the melting points of molybdenum (2898 K) and boron (2473 K); that is why for $T_0 = T_{room}$ the synthesis should proceed in the regime of solid-phase combustion. However, as it was shown in [7, 8], chemical interaction in the system molybdenum – boron cannot be considered to be completely solid-phase and gas-free, since vapour of the suboxides of molybdenum (MoO_3) and boron (B_2O_2) is present in the combustion front and in the heating zone (due to the presence of oxygen dissolved and adsorbed in the initial powder). These suboxides have a notable effect on the kinetics of mass transfer of the reagents and on the formation of the reaction surface. Mass transfer from one component to another may be accelerated for the case of solid-phase reactions by decreasing the size of reacting particles as a result of mechanical action. On the one hand, MA changes the powder morphology, causes an increase in the reaction surface; on the other hand, it causes an increase in the number of structural defects, which results in an increase in the mean absorbed energy; in turn, this leads to an increase in the reactivity. These factors together promote lowering of the activation barriers for the reactions.

The goal of the present work was to investigate the effect of the regimes of MA of initial reagents on the reactivity of Mo–10 % B mixture, to determine optimal activation regimes for which the mixture exhibits maximal reactivity sufficient to obtain high-quality composite materials according to the technology of force SHS compacting.

EXPERIMENTAL PROCEDURE

Molybdenum powder with particle size <5 μm and boron (amorphous brown) smaller than 1 μm. Activation was carried out in AIR-0.015.00.00.000RE planetary mill in the air medium in tightly closed cylinders 250 cm^3 in volume, with the centripetal acceleration along the cylinder axis 250 m/s^2. Powder mixtures were treated with different ratios of the masses of balls (B) and the mixture (M) according to regimes 1 and 2, which differ by a factor of 2 in the ball to mixture mass ratio (the ball mass for regime 2 is two times larger than that for regime 1). Duration of MA was varied within the range 1–15 min. In order to determine heat evolution and the rate of heat evolution, the final mixtures were burnt through in the atmosphere of argon in the reaction chamber of a fast-operating combustion calorimeter BKS-4 [9]. To provide reliable initiation of combustion process, igniting mixture Ni + 32 % Al was used. Calculation of T_{ad} values was carried out using TERMO programme [10]. Investigation of the dependence of combustion rate on initial temperature was carried out in the atmosphere of argon using the reaction chamber equipped with the system of computer registration of thermal emf, the systems of video observation and video recording on the basis of MV-D752 fast-operating camera and image-capturing board (PhotoFocus) SiSo Microenable III with the software. The samples for combustion experiments were prepared from the mixtures activated in the optimal regime and non-activated one. The density of the samples was 0.55 % of the density of the compact material. The analysis of the phase composition of the mixture was carried out with a DRON-3 diffractometer. Specific surface was measured using BET procedure with GKh-1 gas meter. The structure of powder and combustion products was examined with the help of electron focused-beam microscopy using EOS RNI-680 and JSM-35CF instruments. Compact samples were prepared using the technology of force SHS compacting. In doing this, to ensure minimal residual porosity, optimization of the main process parameters was carried out: delay time, exposure, compacting pressure.

RESULTS AND DISCUSSION

Calorimetric investigation showed that the amount of heat released during the reaction is strongly dependent on the parameters of MA: time and B : M ratio. Heat evolution in the mixture activated in regime 1 (Fig. 1) increases within 15 min; further increase in the time of MA does not result in a substantial increase in heat evolution; it remains at a level of ≈400 J/g. This is connected with the fact that small transformation degree is observed; combustion proceeds within a narrow layer of the mixture in the vicinity of igniting mixture. Investigation of the activated mixture by means of X-ray

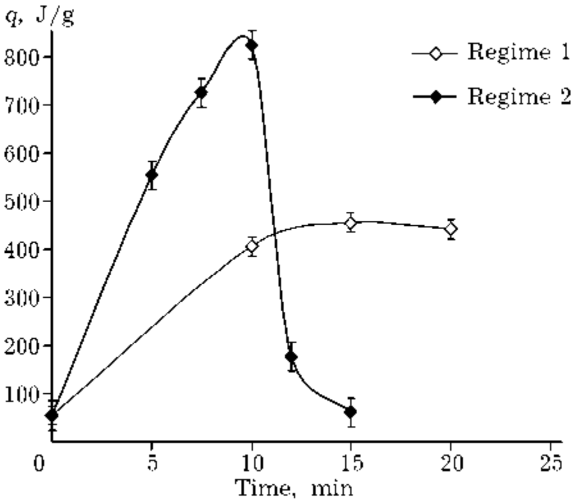

Fig. 1. Dependence of heat evolution q on MA time.

phase analysis (XPA) did not reveal the formation of reaction products, which allowed us to increase the MA load by a factor of 2. According to the data shown in Fig. 1, one can see that the mixture activated in regime 2 exhibits maximal reactivity, after MA for 10 min the amount of heat evolved is 840 J/g. No formation of products was observed by means of XPA. It may be assumed that a decrease in heat evolution after 10 min occurs as a result of parptial reaction of the products during MA. However, the amount and particle size of the formed product are too small to be identified by means of X-ray structural analysis.

Investigation of the effect of the time of MA on specific surface of the mixtures (Fig. 2) showed that the dependence is extremal; the maximal values on the curves of heat evolution and specific surface are observed for the same MA time which is equal to 10 min for regime 2 and 15 min for regime 1. During activation of the mixture, the initial particle size decreases to a definite critical value corresponding to the largest specific surface; after that, particle agglomeration starts, which also follows from the analysis of powder structure (Fig. 3).

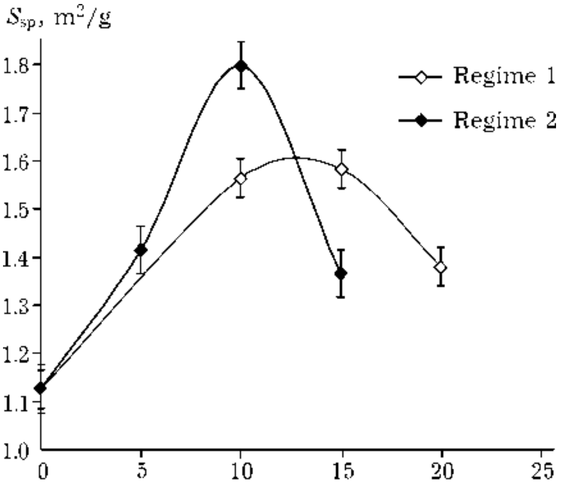

Fig. 2. Dependence of specific surface on MA time.

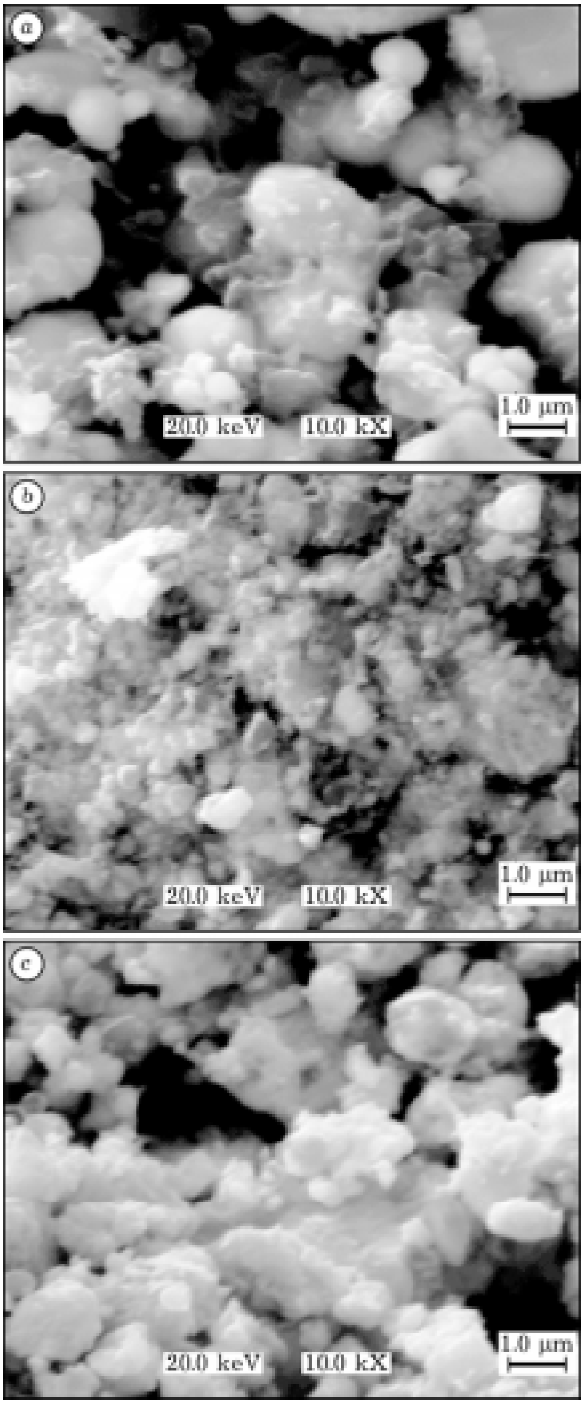

Fig. 3. Microstructure of the mixture. MA time, min: 0 (*a*), 10 (*b*), 15 (*c*).

The initial mixture is composed of spherical molybdenum particles 3–5 μm in size and smaller boron powder (<1 μm) (see Fig. 3, *a*). After treatment for ten minutes (regime 2) the particles of irregular shape smaller than 1 μm are observed (see Fig. 3, *b*); with an increase in the treatment time up to 15 min porous agglomerates 3–5 μm in size are formed (see Fig. 3, *c*). They are composed of the particles with a size about 1 μm. An optimal state of the structure before SHS corresponds to a definite particle size and definite dislocation structure of the metal. Because of this, in order to estimate the effect of MA on the structure of the material by means of XSA, we measured the coherent lengths (CL) and the size of microdeformations of Mo lattice for the initial and activated mixtures. Similar measurements for boron were not carried out because amorphous boron was used in the investigation. The results of investigations are shown in Table 1.

One can see that in both regimes an increase in MA time is accompanied by a decrease in CL. The value of microdeformations of molybdenum lattice for the sample activated in regime 1 remains almost unchanged. Quite contrary, in the case of regime 2 microdeformation increases from 0.05 to 0.53 %, which causes an increase in energy accumulated due to mechanical treatment.

The contribution from MA into the kinetics of combustion process, activation energy (E) was calculated using the equation of heat evolution rate in the approximation considering combustion to proceed according to the mechanism of reaction diffusion through a layer of the formed product; calculation was carried out using the procedure described in [11]:

$$\Delta E = RT\ln(\Phi_2/\Phi_1) \quad (1)$$

where ΔE is the change in activation energy, R is gas constant, T is adiabatic combustion temperature, Φ_1 is the rate of heat evolution for non-activated mixture, Φ_2 is the rate of heat evolution for the mixture activated under optimal conditions.

According to these calculations, a decrease in the activation energy of combustion in Mo–10 % B mixture activated preliminarily under optimal conditions (regime 2, MA for 10 min) is (24± 5) kJ/mol. Mechanical activation of the solid reagents causes a substantial increase in heat evolution during the combustion reaction (see Fig. 1) and, which is especially important, it also causes an increase in heat evolution rate (Φ), which increases more than 3 times in comparison with the initial mixture. The rate of heat evolution was determined from thermograms of the calorimetric analysis. Two curves recorded with BKS instrument are shown in Fig. 4. The first peak corresponds to cooling of the reaction chamber heated preliminarily in a thermostat to a constant temperature, while the second one relates to heat evolution as a result of combustion of a mixture of molybdenum with boron. Heat evolution rate was calculated form thermograms

TABLE 1

Changes in the coherent length (D) and microstrain values (ε) for molybdenum

MA time, min	Regime 1		Regime 2	
	D, nm	ε, %	D, nm	ε, %
0	300 ± 20/0.05 ± 0.01			
5	60 ± 12	0.15 ± 0.01	40 ± 9	0.17 ± 0.01
8	36 ± 7	0.20 ± 0.02	24 ± 4	0.20 ± 0.02
10	30 ± 5	0.22 ± 0.02	20 ± 3	0.22 ± 0.02
12	25 ± 4	0.25 ± 0.02	18 ± 2	0.30 ± 0.03
15	21 ± 3	0.30 ± 0.03	17 ± 2	0.53 ± 0.05

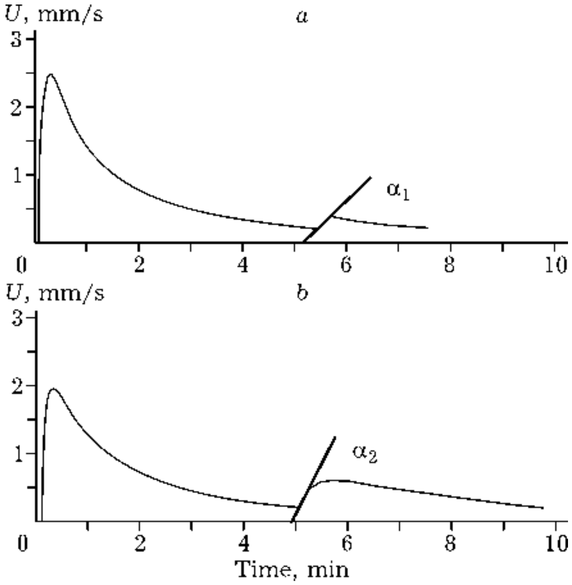

Fig. 4. Thermograms of activated and non-activated mixtures. α_1 – non-activated mixture; α_2 – activated mixture.

as a tangent of the angle (tg $\acute{\alpha}$) between the tangent to the second peak and the axis of time.

Activation energy was also estimated using the conventional procedure involving Arrhenius equation (2). For this purpose, the dependence of combustion rates for the initial and activated mixtures was plotted against the initial temperature (T_0) (Fig. 5). In order to determine activation energy, the experimental dependencies were obtained in the coordinates ln $U(T_0)$. This allowed us to calculate effective kinetic parameters (3), (4):

$$k = Ae^{-E/RT} \quad (2)$$

$$k = \mathrm{d}\ln U/\mathrm{d}T_0 \quad (3)$$

$$E = 2RT_c^2k \quad (4)$$

where k is temperature coefficient of combustion rate, U is combustion rate, T_0 is initial temperature, T_c is combustion temperature, R is the absolute gas constant, E is activation energy.

The experimental investigation showed that combustion rate of non-activated mixture is much higher than that of the initial mixture. An unexpected phenomenon of substantial interest is the occurrence of a broken curve on the $U(T)$ plot (see Fig. 5), which is an evidence of the change of the mechanism of reagent mass transfer and the combustion mechanism in general. For the mixture after MA in the optimal regime, the curve consists of two regions: at the first of them, for T_0 <600 K, the activation energy E_2' is ≈ (191 ± 6) kJ/mol, at the second one it is E_2'' ≈ (780 ± 90) kJ/mol. It should be noted that the E_2' value is less than the corresponding value for the initial mixture E_1 ≈ (229 ± 14) kJ/mol. The difference $\Delta E = E_1 - E_2$ is 30 kJ/mol, which is in good agreement with the value calculated using equation (1).

An increase in combustion rate for the activated mixture can be explained, on the one hand, by a substantial increase in its specific surface (see Fig. 2) as a result of extensive grinding of molybdenum particles under the action of milling bodies, on the other hand, by an increase in the concentration of oxygen bound and adsorbed on molybdenum particles. The latter fact is due to mechanical activation carried out in the air. Mass transfer through the gas phase makes a contribution into an increase in the combustion rate. According to [7], the presence of some amount of MoO_3 in the mixture causes enhancement of the role of exothermal reaction (1) in the combustion process; this reaction is parallel to the main one (in which molybdenum reacts directly with boron) and helps increasing the rate of the process

$$3B(sol.) + MoO_3(g.) \rightarrow MoB(sol.) + B_2O_3(sol.) \quad (1)$$

One can see from Fig. 6 that for T_0 above 600 K combustion temperature increases. This causes an increase in the partial pressure of MoO_3 vapour and rapid disappearance of the oxide film from the highly developed (in comparison with non-activated mixture) surface of molybdenum particles, a decrease in the

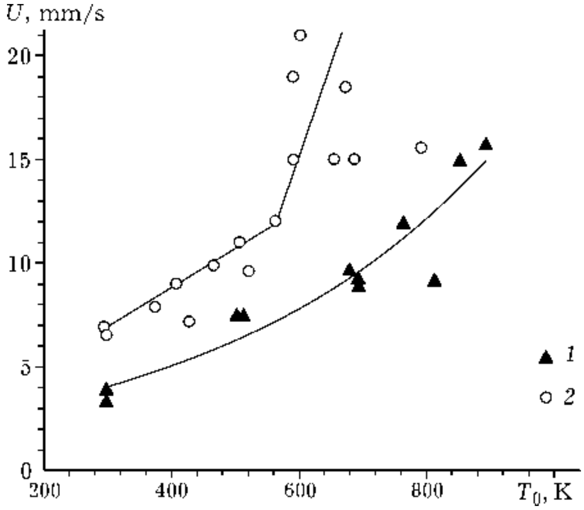

Fig. 5. Dependence of combustion rate on the initial temperature. Here an in Figs. 6, 7: *1, 2* – regimes 1 and 2, respectively.

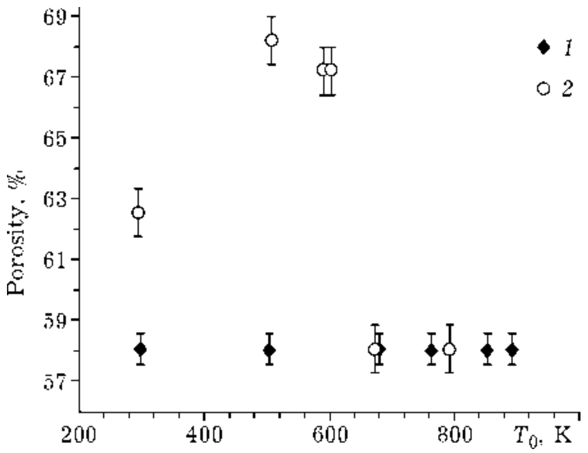

Fig. 6. Dependence of porosity of the material after combustion on the initial temperature. For designations, see Fig. 5.

effect of the gaseous reagent on combustion rate; thus, the interaction proceeds mainly according to the mechanism of solid-phase reaction diffusion. The activation energy of combustion process E_2' increases sharply from ≈(191 ± 6) kJ/mol to $E_2'' \approx (780 \pm 90)$ kJ/mol, which explains the presence of the second region of the broken curve for the mixture after MA (see Fig. 5).

An indirect confirmation of the mechanism described above is the fact that the combustion of samples composed of activated mixture is accompanied by a substantial increase in their volume as a result of intensive gas evolution (see Fig. 6) within the temperature range from 298 to 600 K, corresponding to the first region of the MA curve (see Fig. 5). At the same time, for $T_0 > 600$ K almost no changes in the sample volume are observed (porosity remains at the same level), similarly to the case of the sample of the initial (non-activated) mixture.

The combustion temperature exhibits a weak trend to increase (Fig. 7) with an increase in T_0; it is lower for the activated mixture than for the non-activated one. According to [8], this fact can be connected with the presence of boron oxide B_2O_3 in the mixture; it acts as a thermal ballast decreasing the combustion temperature. So, MA of this system allows, first, to decrease the size of reacting particles (especially those of molybdenum) thus increasing the reactive surface; second, to increase the reactivity of the Mo–B mixture due to the accumulated energy realized in the plastic deformation and microstrain, third, to change oxygen content, which allowed one to increase the combustion rate.

Having established the optimal activation regimes according to the technology of force SHS compacting, we synthesized low-porous composite targets foe magnetron sputtering. To compare microstructure, density and hardness, a similar material was obtained form the non-activated mixture. When obtaining the composite, to minimize the residual porosity we used a mixture Ti + 14 % B + 11 % C as a chemical furnace. This mixture provided additional heating of the exothermal layer.

The structures of fractures of MoB targets are shown in Fig. 8. The structure of the materials is fine granular. The grain size of the sample obtained without MA (see Fig. 8, *a*) varies within rather broad range from 1 to 5 μm, which is comparable with the size of the initial powder (see Fig. 3, *a*) and points to thermal and structural non-homogeneity of the front of combustion wave. The material is at the stage of growth of the contact necks and closure of the through porosity. This is an

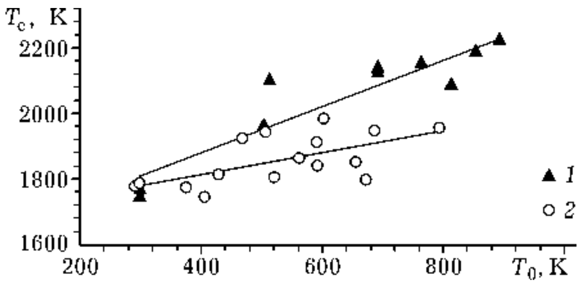

Fig. 7. Dependence of temperature of the combustion process on the initial temperature. For designations, see Fig. 5.

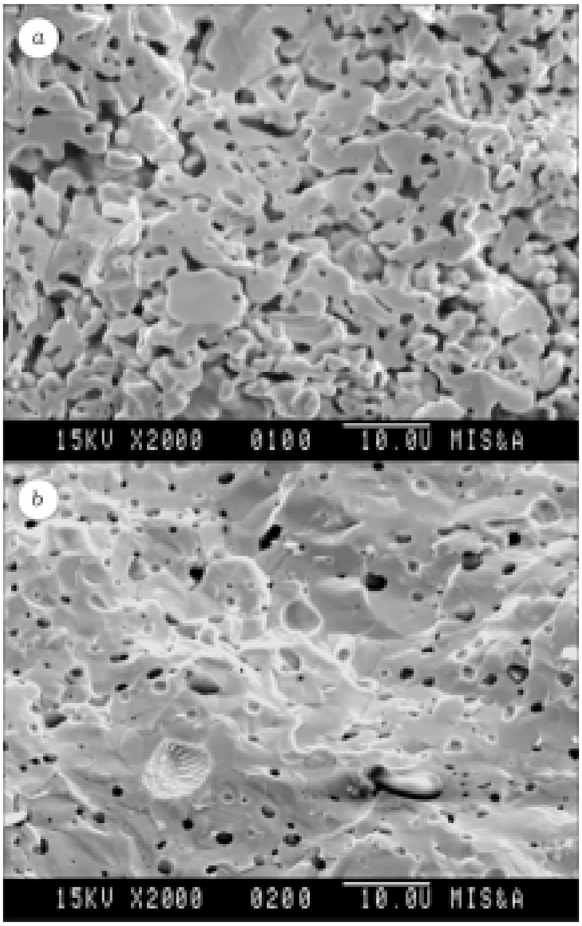

Fig. 8. Microstructure of the material obtained according to the technology of force SHS compacting from non-activated mixture (*a*) and activated one (*b*).

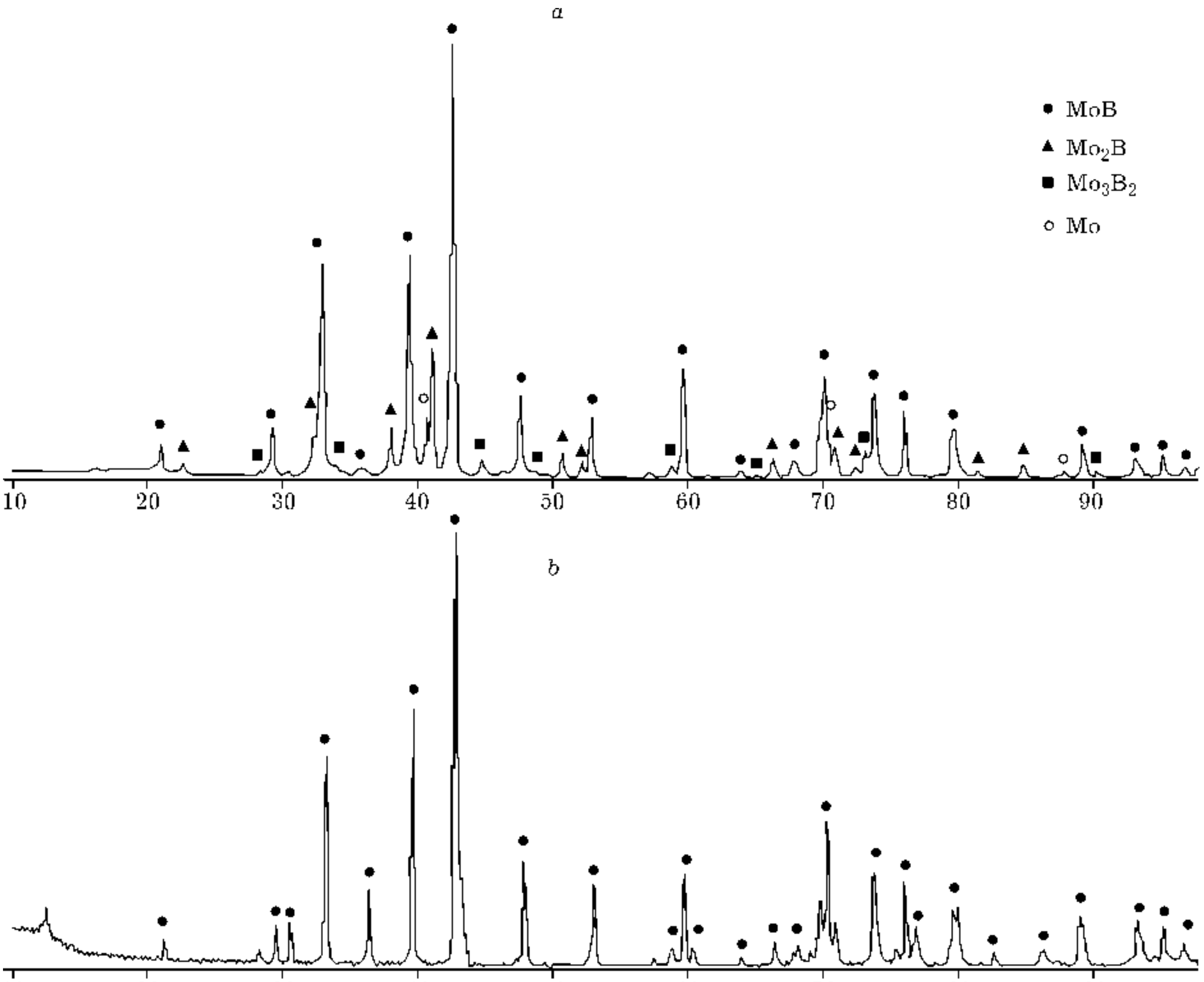

Fig. 9. Diffraction patterns of the material synthesized from non-activated mixture (*a*) and activated one (*b*).

evidence of incomplete transformation and non-steady combustion regime, which is confirmed by the XPA data. In addition to the main phase MoB, the products contain up to 35 % Mo_2B and Mo_3B_2, as well as unreacted Mo (Fig. 9). The sample contains large number of pores with a size from 1 to 10 μm, and cracks. The length of some of them reaches several ten micrometers. The main reason of the formation of a porous target is, as it was already mentioned, low reactivity of the mixture prepared under the standard conditions of the ball mixer.

The size of MoB grain in the target made of the activated mixture (see Fig. 8, *c*) is about 3–4 μm. The fracture exhibits no elements corresponding to the first stages of the formation agglomerated structure, as it was the case for the target prepared form on-activated powder. This is an evidence of an increase in heat evolution rate and in combustion rate when the activated mixture is used (see Figs. 4 and 5). Mechanical activation leads to an increase in the reactivity of the Mo–B mixture, as it was established previously, and allows one to obtain the material of the required structure. According to the XPA data, the sample consists of MoB by 100 %. Its density is 0.95 of the density of the compacted material, which is larger by 25 % than the density of the material synthesized from non-activated mixture. Pore size is 2–3 μm. The sample is sufficiently dense and uniform; it corresponds to the requirements to targets for magnetron sputtering.

Micro-hardness (HV^{200}) of the composite material made of the activated mixture is (20 ± 3) GPa, while that for the initial mixture is only (9 ± 2) GPa. So, with the MA mixture of the initial components, the density and

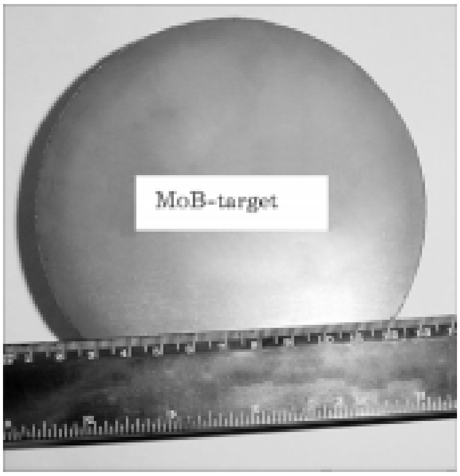

Fig. 10. The appearance of a large-sized multilayer cathode.

hardness of MoB material increased, which comprises a substantial advantage of the resulting material.

Using the technology of SHS compacting, large-sized planar target cathodes for magnetron sputtering with the MoB working layer were obtained (Fig. 10).

CONCLUSIONS

1. It is shown that preliminary mechanical activation of a Mo–B mixture allows one to increase the combustion rate as a result of a substantial decrease in the size of reacting particles (especially those of molybdenum), increase in the reaction surface and reactivity due to the accumulated energy realized in plastic deformation and microstrain, as well as due to an increase in the concentration of bound and adsorbed oxygen.

2. For the activated mixture, a change of the combustion mechanism was discovered; it manifests itself as a substantial increase in the activation energy.

3. High-quality composite target cathodes with the working layer made of MoB for vacuum spraying technology were obtained.

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