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Mo–Nb–Si–B Alloy: Synthesis, Composition, and Structure

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Abstract: Cast refractory alloys Mo–Nb–Si–B were prepared by centrifugal self-propagating high-temperature synthesis (SHS) from metallothermic mixtures containing MoO_3, Nb_2O_5, Al, Si, and B powders, and additive of Al_2O_3 as a temperature-moderating and chemically inert agent. Variation in the centrifugal acceleration and amount of the additive affected the composition and structure of cast Mo–Nb–Si–B alloys. In a wide range of values, the combustion temperature was found to exceed 3000 K, and the combustion products were obtained as two-layer ingots of target Mo–Nb–Si–B alloy (lower) and Al_2O_3 slag (upper).

Keywords: combustion; self-propagating high-temperature synthesis (SHS); Mo-based cast alloy

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1. Introduction

Mo–Si alloys have high resistance to oxidation in air at temperatures of 1000–1650 °C; however, at the intermediate temperatures of 600–800 °C, they are prone to catastrophic oxidation [1,2]. The addition of B makes it possible to form a dense borosilicate glass that protects ceramics against oxidation. Mo–Si–B alloys prepared by heating and subsequent cooling were shown in [3] to represent Mo-based solid solution with Mo_3Si and/or Mo_5SiB_2 inclusions. These alloys possess a far greater oxidation resistance than previously known molybdenum ones, but they are not as good as Mo_5Si_3–Mo_3Si–Mo_5SiB_2 alloys [4], and yet they contain a plastic α-Mo phase. As mentioned in [5], varying the volume fraction and morphology of the α-Mo phase in these Mo–Mo_3Si–Mo_5SiB_2 intermetallics allows it to achieve high values of fracture toughness and creep strength. Additional doping with Nb strengthens the molybdenum matrix but leads to no changes in the structural composition [6,7].

Mo–Si–B or Mo–Nb–Si–B alloys manufactured by the powder metallurgy method exhibit high heat resistance and high-temperature strength, thereby having the potential for turbo-engine applications. Because of the high melting points of Mo–Si-based alloys, multistage methods of powder metallurgy are favorable over melting ones. One of them includes the following stages: (1) mechanical activation in a vertical attritor, for 10 h, to completely dissolve Nb, Si, and B in the Mo matrix; (2) sintering at 1450 °C, and (3) hot isostatic pressing (HIP) at 1500 °C and under a pressure of 200 MPA [8]. An alternative route is the cost-effective, productive, and environment-friendly centrifugal self-propagating high-temperature synthesis (SHS) process, which provides the synthesis of Mo–Nb–Si–B alloy from a mixture consisting of a thermite composition MoO_3/Nb_2O_5/Al/Si/B and an elemental composition Mo/Nb/Si/B, such as a temperature-moderating additive [9]. In this work, we added Al_2O_3 instead of the costly and scarce Mo and Nb.

Thus, this work aimed at the preparation of Mo–Mo_3Si–Mo_5SiB_2 alloy by centrifugal SHS of MoO_3–Nb_2O_5–Al–Si–B powder mixtures containing Al_2O_3 as a temperature-moderating agent with special emphasis on optimizing process conditions.

2. Thermodynamic Calculation

Table 1 shows the composition of the green mixture and nominal weight percentage of elements (Mo, Si, B, and Nb) in a combustion product.

Table 1. Composition of the green mixture and nominal weight percentage of elements in a combustion product (wt %).

	Mo	Si	Nb	B	MoO_3	Nb_2O_5	Al
Green mixture	–	1.5	–	0.5	68.9	2.4	26.7
Combustion product	92.5	3.0	3.4	1.0	–	–	–

Thermodynamic calculation (Figure 1a, where *P* is mass fraction of phases in combustion products), carried out using the software package TERMO 2.0, ISMAN, Chernogolovka, Russia [10], showed that the combustion of $MoO_3/Nb_2O_5/Al/Si/B$ mixture occurs at high temperatures in the range of 2225–3500 K, at which condensed combustion products—alloy (Mo–Nb–Si–B) and slag (Al_2O_3)—are in a liquid phase state.

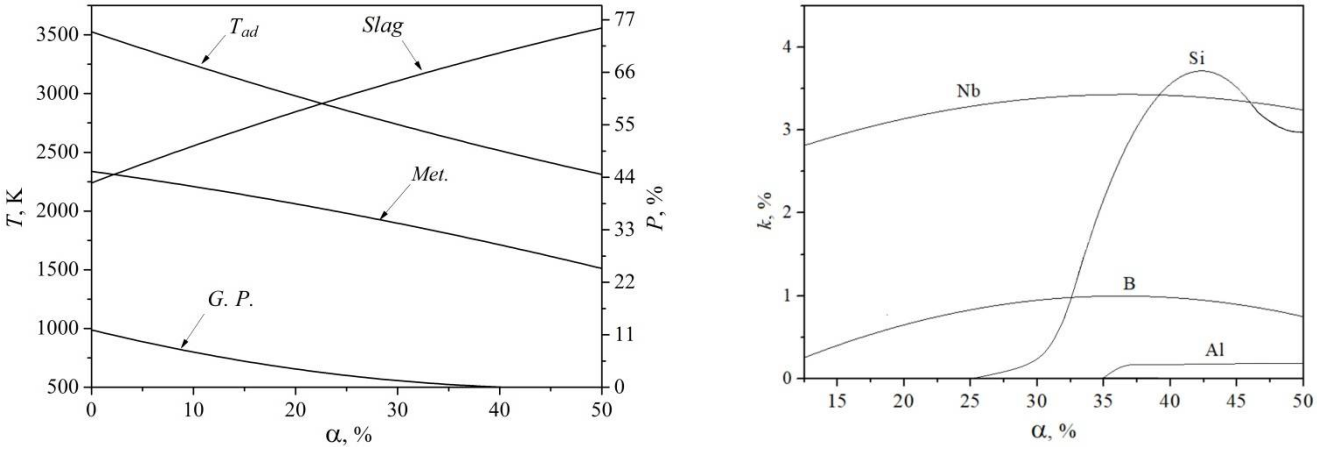


Figure 1. (**a**) Combustion temperature (*T*), mass fraction of phases in combustion products (*P*), and (**b**) percentage of constituents (the rest Mo) in metal phase (*k*) as a function of α. Here, T_{ad} is the adiabatic temperature and G.P. is the gas phase.

Thermodynamic consideration predicts the formation of up to 10 wt % (*P*) of gaseous Al_2O, BO, B_2O_2, SiO_2, NbO_2, and so on (Figure 1a). The addition of aluminum oxide (α) to green composition decreases the combustion temperature *T* and mass fraction *P* of gas phase, as well as contributing to the appearance of B and Si in the combustion products (Figure 1b, where *k* is the percentage of constituents in the metal phase).

3. Experimental

Green mixtures containing powders of MoO_3, Nb_2O_5, Al, Si, and B in the amount of 40 g were ignited in a quartz tube (25 mm in diameter, 70 mm high) using a centrifugal machine described in [11] at the centrifugal acceleration a = 1–400 g.

In our experiments, the burning velocity U, the material loss (η_1) caused by sputtering, and the yield of target metallic phase into ingot η_2 were calculated using the following relationships:

$$U = h/t \quad (1)$$

$$\eta_1 = [(m_1 - m_2)/m_1] \times 100\% \quad (2)$$

$$\eta_2 = (m_{exp}/m_{cal}) \times 100\% \quad (3)$$

where h is the mixture height, t is the burning time, m_1 is the mass of green mixture, m_2 is the mass of combustion product, and m_{exp} and m_{cal} are the experimental and calculated mass of metallic ingot, respectively. m_{cal} was worked out on the basis of chemical equation with the complete alumothermal reduction of initial oxides and alloying elements (Si and B) in the corresponding weighed portions.

The combustion products were characterized by scanning electron microscopy SEM (Carl Zeiss Ultra Plus microscope, Carl Zeiss, Jena, Germany) and X-ray diffraction analysis XRD (DRON-3M diffractometer, Cu-K_α radiation, Burevestnik, St. Petersburg, Russia). Concentrations of Mo, Nb, Si, and Al in the final product were determined by spectrophotometry. The determination of boron was carried out by potentiometric titration of mannitol-boric acid, while that of oxygen was performed by reductive melting in an inert carrier gas flow. The Vickers hardness of the synthesized samples was measured using a 100 g load and a 15 s loading time (Instron 402MVD tester, Wilson Instruments, Norwood, MA, USA).

4. Results

The experiments showed that the combustion of high-exothermic mixture is accompanied by the splashing of burning products. This was suppressed by the introduction of Al_2O_3 (α) into the mixture and forces of artificial gravity. The mixtures were found to burn within the range α = 0–50%. As α increased within the indicated range, material loss η_1 significantly decreased, as seen in Figure 2. The cast product was formed for α = 0–40%. In this case, the combustion products were prepared as two-layer ingots: Mo–Nb–Si–B target alloy (lower) and Al_2O_3 slag (upper).

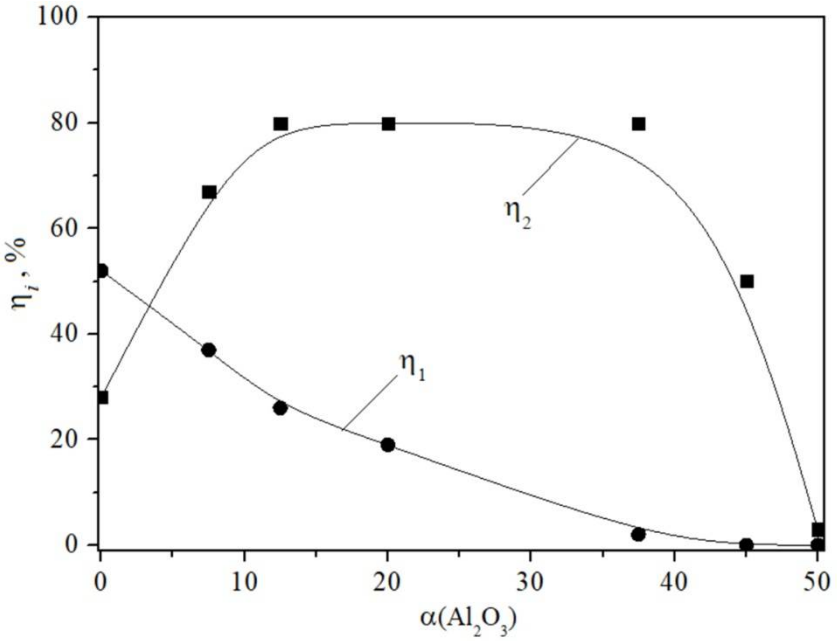


Figure 2. The values of η_1 иη_2 as a function of α (m_1 = 40 g, a = 40 g).

As shown in Figure 3, the action of gravity forces makes it possible to increase the product yield η_2 from 80 to 90 wt %. An additional point to emphasize is that, as a/g grows, the amount of pore space in the resultant cast Mo–Nb–Si–B material, according to microstructural analysis, decreases. For a > 100 g, a pore-free structure is formed.

Figures 4 and 5 illustrate the influence of α and a/g on the percentage of constituents (k) of cast Mo–Nb–Si–B material, respectively. For α = 10–40% and a = 40–400 g, EDS analysis for Nb gives 2–2.5 wt %, which is lower than the calculated value. The measured contents of Si and B show the values close to nominal ones (3–3.5 and 1 wt %, respectively).

With increasing α and a/g, Al concentration is seen to decrease from 6 to 2 wt %. The content of the main element (Mo) is within the range of 85–90 wt %.

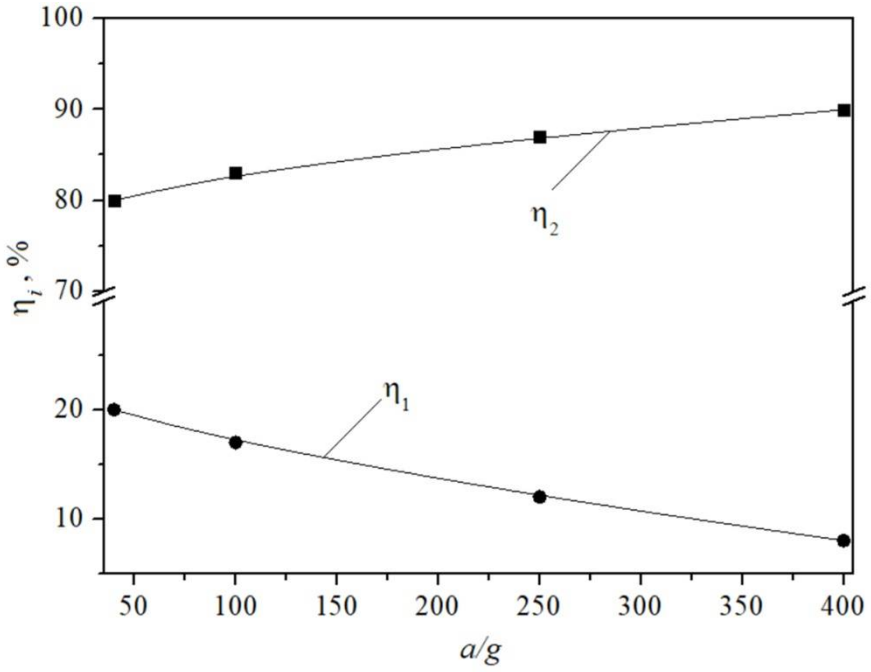


Figure 3. The values of η_1 and η_2 vs. a/g (m_1 = 40 g, α = 20 wt %).

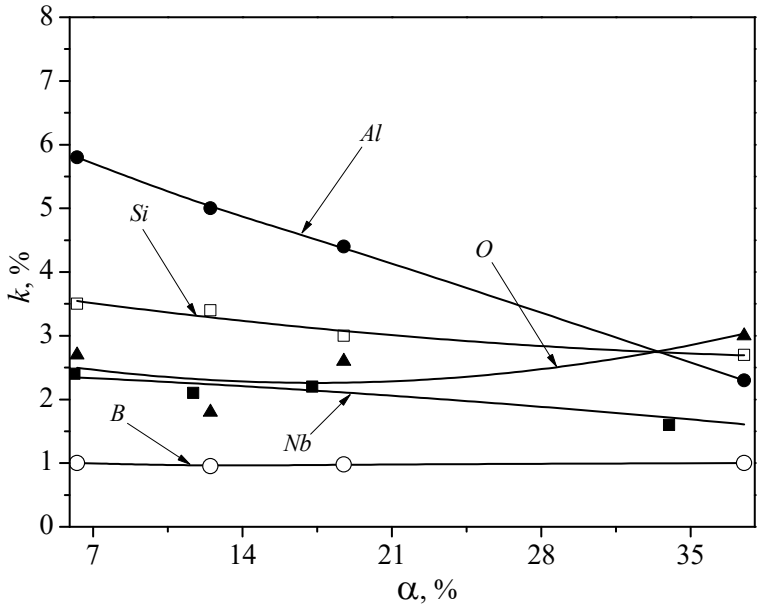


Figure 4. The percentage of constituents (k) in the resultant cast Mo–Nb–Si–B material as a function of α (m_1 = 40 g, a = 40 g).

The XRD pattern of Mo–Nb–Si–B ingot collects the peaks belonging to the following phases: (1) α-Mo, (2) Mo_3Si, and (3) Mo_5SiB_2 (Figure 6a).

No other reacted phases were found. It is pertinent to note that XRD analysis shows no peaks of Nb insofar as it was completely dissolved in the Mo matrix phase during synthesis. A Mo/Si ratio in Mo_3Si is 91.1/8.9 (wt %), while a Mo/Si/B ratio in Mo_5SiB_2 is 90.6/5.3/4/1. The slag is seen in Figure 6b to contain Mo in addition to conventional phase (Al_2O_3). Optic metallography confirmed the presence of individual spherical Mo particles in the oxide layer. Within the ranges α = 0–10% and α = 40–50%, there is a high

Mo content that favors the formation of a metal–ceramic structure in the slag layer. Thus, α = 10–40% was chosen as optimal.

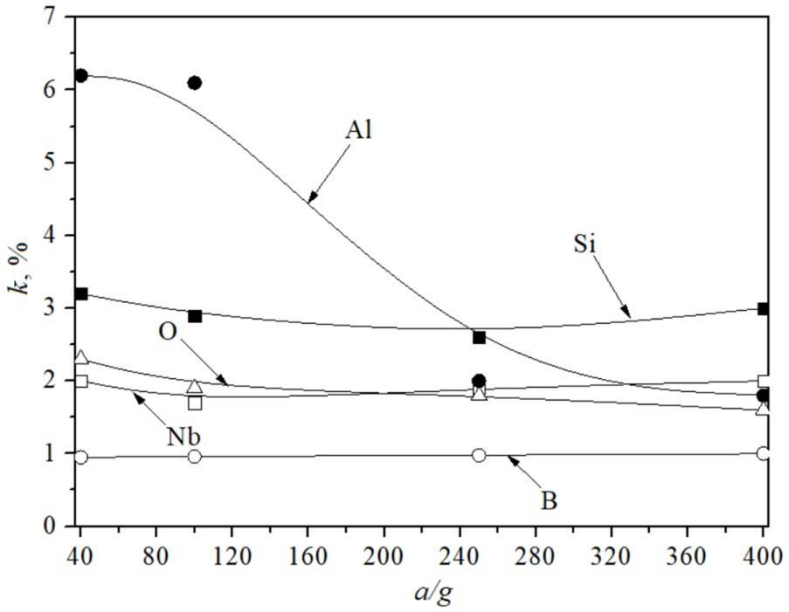
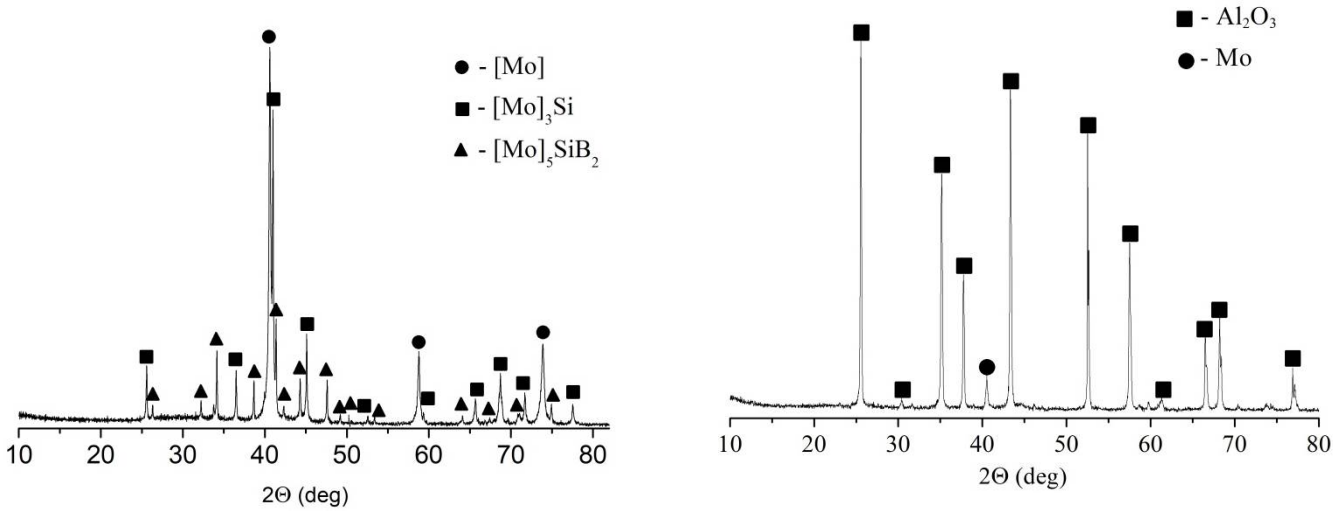


Figure 5. The percentage of constituents (k) in the resultant cast Mo–Nb–Si–B material as a function of a/g (m_1 = 40 g, α = 20 wt %).

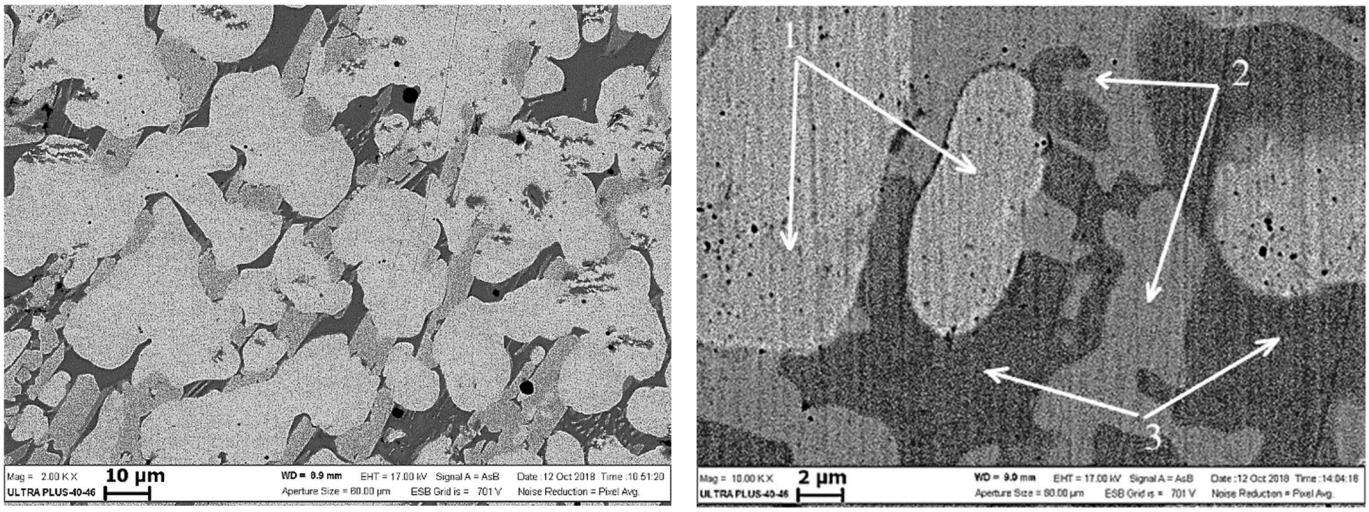


(**a**) (**b**)

Figure 6. Diffraction patterns of (**a**) metallic phase and (**b**) slag derived from a = 100 g and α = 20 wt %.

The SEM images presented in Figure 7 show a cast structure consisting of Mo solid solution (marked in Figure 7b by 1) and two intermetallic phases, Mo_3Si and Mo_5SiB_2 (2 and 3, respectively). A quantitative analysis by X-ray diffraction revealed that the main phase is Mo_3Si; its volume fraction approximates 40%. α-Mo phase has a volume fraction of around 30%, and, as seen in Figure 7a, forms to be discontinuous. According to [5], this fact can positively affect the creep strength of Mo–Mo_3Si–Mo_5SiB_2 intermetallics.

In order to evaluate the mechanical properties, we measured the Vickers hardness of ingots derived from a = 100 g and α = 20 and 30 wt %. For α = 20 wt %, the average hardness value was 1350 HV. It is 80 HV lower than the hardness of ingot prepared at α = 30 wt %.



(**a**) (**b**)

Figure 7. (**a**) Low- and (**b**) high-magnification SEM (scanning electron microscopy) images of cast alloys obtained at a = 100 g and α = 20 wt %. Magnification: (**a**) Mag 2.00 KX; (**b**) Mag 10.000 KX. Working distance (WD) = 9.9 mm. In (**b**): 1—Mo solid solution, 2—Mo_3Si, and 3—Mo_5SiB_2.

5. Discussion

The process of obtaining Mo-based cast alloys by centrifugal SHS includes 3 stages: (1) the combustion of $MoO_3/Nb_2O_5/Al/Si/B$ highly exothermic mixture and the formation of two-phase—Mo–Nb–Si–B and Al_2O_3—melt; (2) the gravitational separation of melts insoluble in each other under artificial gravity; and (3) the cooling, crystallization, and formation of the composition and structure of Mo–Nb–Si–B and Al_2O_3.

The combustion of $MoO_3/Nb_2O_5/Al/Si/B$ mixture is accompanied by the splashing of burning material. The latter is caused by the formation and release of gas under the action of Archimedean force. Thermodynamic calculation showed (Figure 1a) that up to 10 wt % of the gas phase (G.P.: Al_2O, BO, B_2O_2, SiO_2, NbO_2, and so on) can be formed. The introduction of Al_2O_3 into green mixture reduces gas formation, thereby markedly suppressing the splashing of mixture. However, as Al_2O_3 content increases, the combustion temperature decreases (see Figure 1a) and, as a result, the starting mixture loses its ability to burn.

The completion of the combustion results in a continuous Al_2O_3 melt containing Mo–Nb–Si–B drops. Under the action of gravity forces, heavy drops move to the bottom of the quartz mold and form a metal layer. The completeness of gravitational separation is determined by the ratio of velocities of the drops and the cooling of melt. Drop velocity is determined by the value of the centrifugal acceleration.

Under optimal conditions (α = 20–30% and a > 100 g), it is possible to suppress the splashing and to progress to 90 wt % of the yield of the target product (see Figure 3).

At the final stage of centrifugal SHS, the metal layer containing Mo–Nb–Si–B-based solid solution and two phases of Mo_3Si and Mo_5SiB_2 are formed. SHS-produced Mo–Mo_3Si–Mo_5SiB_2 alloy is characterized by high hardness values, which far exceeds (by approximately 3 times) those attainable in Mo–Nb–Si–B alloy fabricated by a powder metallurgical method (425 *HV*) [7].

6. Conclusions

Mo-based composition materials reinforced with Nb, Si, and B, possessing good high-temperature and heat-resistance properties, can be prepared by centrifugal SHS from the highly exothermic composition $MoO_3/Nb_2O_5/Al/Si/B$ containing temperature-moderating additive (Al_2O_3) under the conditions of artificial gravity. Such materials seem

promising as a candidate for the next generation of high-temperature structural materials and as a high-hardness coating material [12].

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