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The Effect of Mechanical Treatment on the Phase Formation of the Synthesized Material Based on Molybdenum Disilicide

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Abstract

The paper demonstrates the feasibility of obtaining materials based on molybdenum disilicide through the combination of combustion process and shear deformation of the synthesis products. It has been established that mechanical treatment affects combustion processes, phase and structure formation of materials, resulting in the change of grain size, morphology and quality of the finished product. Shear deformation at SHS leads to almost 100 % output of powder of a fineness of less than 500 microns.

Keywords

Mechanical treatment; phase formation; shear deformation; SHS; silicides; synthesis.

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Introduction

Silicides are used in many areas of science and technology to create special technological processes and products with special properties [1]. Silicides of refractory metals, especially molybdenum [2], are widely spread, they are an alternative to special alloys, intermetallics and ceramics [3, 4]. Silicides have a number of unique properties: high heat resistance and thermal resistance, sustainability of mechanical properties in a wide temperature range, higher conductivity, and compatibility of the technologies of silicides' obtaining with the overall technology of final product manufacturing [5].

The implementation of the process of self-propagating high-temperature synthesis (**SHS**) combined with shear deformation of initial components and the resulting combustion products [6] creates opportunities for the development of new materials based on molybdenum disilicide. SHS method [7] is based on the use of internal energy of the initial components. The fact that a self-propagating reaction can occur in a narrow zone constitutes the characteristic feature of the method. This zone moves around the substance due to heat transfer after a local short-term initiation in the initial mixture of reagents. Mechanical treatment leads to mixing of the emerging fine structure and inhibits the processes of crystallization and recrystallization [8]. The deformation parameters of the process, primarily the rate of deformation, have a strong influence on the processes of combustion and structure formation: the change of grain size, shape and arrangement of grains. By changing these parameters in a wide range, the quality of the powder and its morphology can be modified. Various aspects of the effects of mechanical treatment on SHS processes are still poorly understood.

The aim of this work was to study the influence of mechanical treatment on the phase formation of the synthesized materials based on molybdenum disilicide.

Objects and methods of research

Molybdenum and silicon powders were taken as the source component to obtain the finished material based on molybdenum disilicide (Table 1).

Table 1

Mass and mass content, % of source components

Mass content, %	
Mo	Si
63.14	38.86

The synthesis of source components of molybdenum and silicon is carried out as follows:

$$Mo + 2Si \rightarrow MoSi_2 + Q_1.$$

The combustion under this scheme is unstable, flowing in a pulsed mode, wherein the heat of reaction is low (Q_1 = 31.4 kcal/mol). Even a slight excess of silicon or large size of particle of the original component can lead to the termination of the reaction. To improve exothermal properties of the system, the starting powders were pre-heated to a temperature of 350 °C.

The experiments were carried out in a specially constructed rotary viscometer (Fig. 1). A graphite cup was filled in a pre-mixed charge of 30 mm height and then pre-compacted to the height of $0.8h_{in}$. This was done in order to prevent charge straying with the passage of the combustion wave. Then SHS of a tungsten coil U = 40 V was initiated. After the passage of the combustion wave the rotor dropped to the lower base of the graphite cup with constant rotation for 40–60 seconds until the end of a full course of structural transformations in the synthesized charge. The experiments were carried out without rotation of the rotor and at a frequency of rotation of 120 r/min.

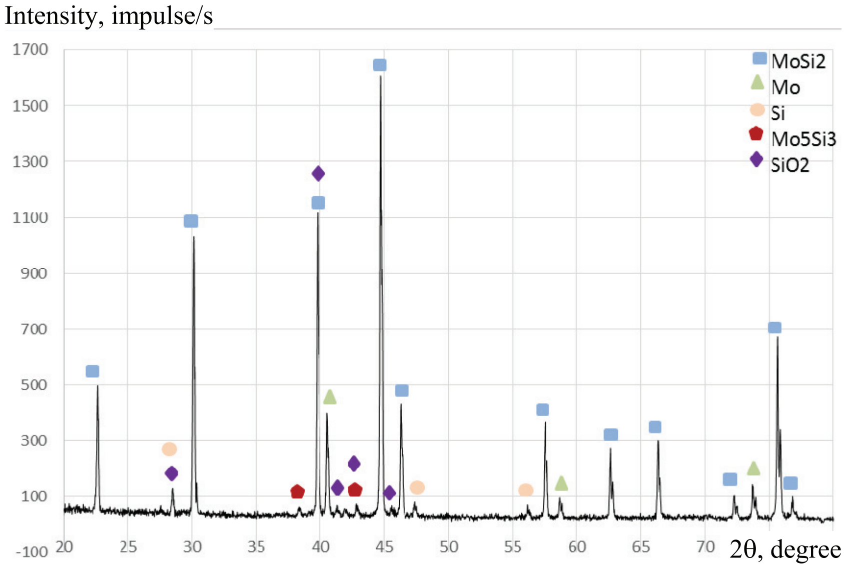
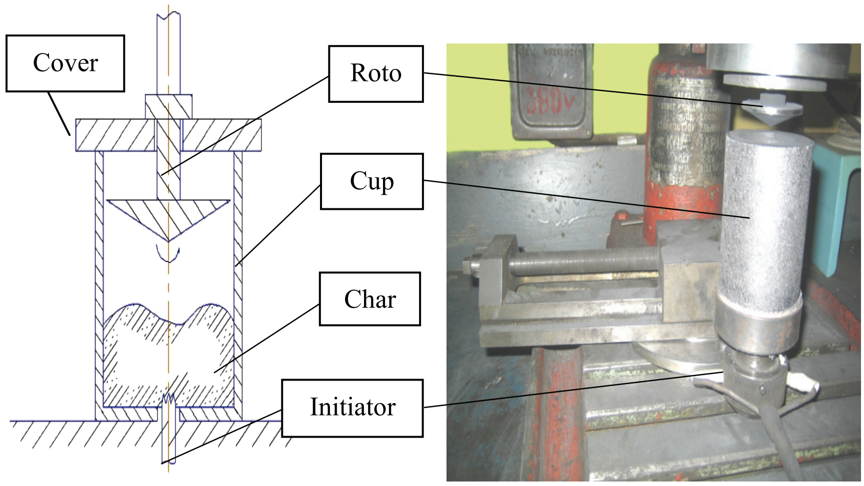


Fig. 2. Radiography of $MoSi_2$ without mechanical treatment



a) *b*)

Fig. 1. Experiment:
a – schematic diagram; *b* – photo of the working part

Experiment and discussion

After the SHS synthesized material consists of the main phase of $MoSi_2$, the lower silicide Mo_5Si_3 (Fig. 2). A characteristic feature of the obtained synthesized material is the presence of unreacted starting powder of molybdenum and silicon. This is mainly observed in the areas of contact with the cup walls. Due to weak exothermic properties of the reaction and intensive conductive heat removal in the reactor, combustion near the wall fades and the synthesis fails. This is confirmed by the XRD: the radiograph shows characteristic peaks of the original components of molybdenum and silicon. Also the x-ray shows the peaks of SiO_2, suggesting that during the synthesis silicon is oxidized.

To determine the effect of mechanical treatment during SHS on phase transformation experiments were carried out on the synthesis of this system, followed by the application of pressure on the combustion products according to the timeline shown in Fig. 3, where t_c is the time of passage of the combustion wave, t_d is the delay time before mechanical treatment, and t_m is the time of mechanical treatment of the synthesized material.

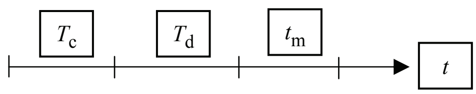
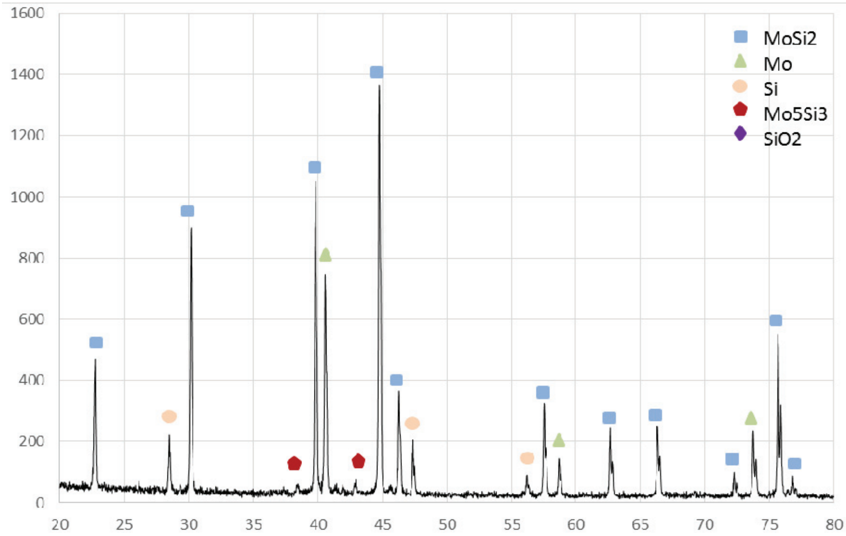


Fig. 3. The experiment's time scale

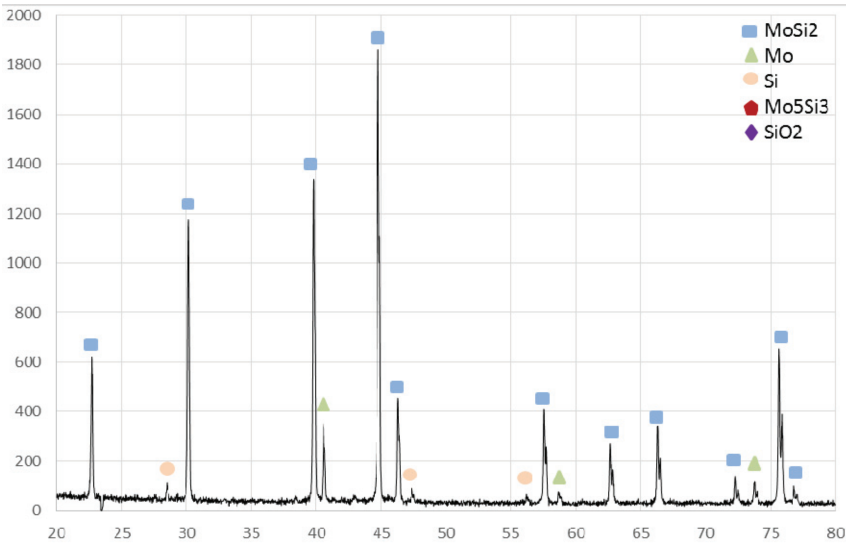
Intensity, impulse/s



2θ, degree

Рис. 4. Radiography of $MoSi_2$ after the mechanical treatment at $t_d = 0$ s

Intensity, impulse/s



2θ, degree

Fig. 5. Radiography of $MoSi_2$ after the mechanical treatment at $t_d = 5$ s

Table 2

The content of the phases in the synthesized materials, mass content, %

Obtained material	$MoSi_2$	Mo	Si	SiO_2	Mo_5Si_3
SHS without mechanical treatment	68	15	6	7	4
SHS with mechanical treatment ($t_d = 0$ s)	62	26	10	–	2
SHS with mechanical treatment ($t_d = 5$ s)	84	12	4	–	–
SHS with mechanical treatment ($t_d = 10$ s)	87	11	2	–	–

The first series of experiments consisted in the application of mechanical treatment immediately after the passage of the combustion wave ($t_d = 0$ s). Fig. 4 shows its X-ray diagram. The synthesized material, same as without mechanical treatment, includes a main phase of $MoSi_2$, the lower silicide Mo_5Si_3, and there is unreacted raw material powder of molybdenum and silicon.

The second series of experiments consisted in the application of mechanical treatment with time delay. For example, Fig. 5 shows the X-ray diagram when the delay time $t_d = 5$ s. In the resulting material, the main phase is $MoSi_2$, and the lower silicide Mo_5Si_3 was not detected. The material includes unreacted raw material powder of molybdenum and a small amount of silicon. Silicon oxide is not detected. This suggests that in the reactor the oxygen supply from the outside is limited.

Quantitative X-ray phase analysis showed (Table 2) that the highest content of the main phase of $MoSi_2$ (84 %) is contained in the material subjected to mechanical treatment. Besides, when the delay time is increased from 5 s to 10 s the proportion of $MoSi_2$ also increases up to 87 %; at the same time the proportion of the source component reduces and the lower silicide Mo_5Si_3 and oxides are not formed. The synthesized material obtained through SHS without this treatment contains $MoSi_2$ in the amount of 68 %. Compared to the previous samples, there is a larger amount of the initial powder in the synthesized material: 15 % of molybdenum and 6 % of silicon, also there is 4 % of the lower silicide Mo_5Si_3. Thus, when a mechanical treatment is applied to the synthesized material, its phase formation presents a more complete process, compared with the material obtained by SHS without mechanical treatment. The results show that applying the mechanical treatment is required at a certain time delay, which leads to a more complete phase formation of the synthesized material.

After the chemical reaction various physico-chemical post-processes occur in the SHS product. Hot porous material is compacted under the external pressure, a structural frame is formed of the individual particles, the material is undergoing sintering and cooling of combustion products associated with the cooling. In addition, the material's structure and phases are formed, crystallization and recrystallization are in process. Contact grains of a crystalline substance thus form a common border. Intergranular contact is expanding, the process of grains' coalescence is evolving. The development of this process depends on the presence of liquid, which separates the adjacent grains, and on internal and external forces. In the experiment, it is possible to implement different mechanisms of sintering: sintering in the conditions with only internal forces (SHS without mechanical stress) and sintering under external mechanical treatment.

It has been experimentally shown that the competition of these mechanisms of sintering on the background of combustion products cooling leads to the non-monotonous character of the dependence of the crushed products' mass $\Delta M = m_{pwd}/m_{in}$ on delay time before the application of mechanical treatment. The dependence of the crushed mass of products on the delay time before the application of mechanical treatment is depicted in Fig. 6, where m_{in} is the mass of initial backfill, and m_{pwd} is the mass of the powder excluding cakes and agglomerates, sifted through a sieve of 500 μm.

It was found that after SHS without mechanical treatment, the synthesized material consists mostly of agglomerated particles fused with each other. The crushed mass of the powder is not more than 20 %. The same pattern is observed when the delay time of 30 s or more is applied before mechanical treatment. This time having elapsed, the material cools, agglomerates and does not take to mechanical treatment. For subsequent grinding takes more effort. With the decrease of delay time before the application of mechanical treatment the output of powder increases and reaches almost 100 %.

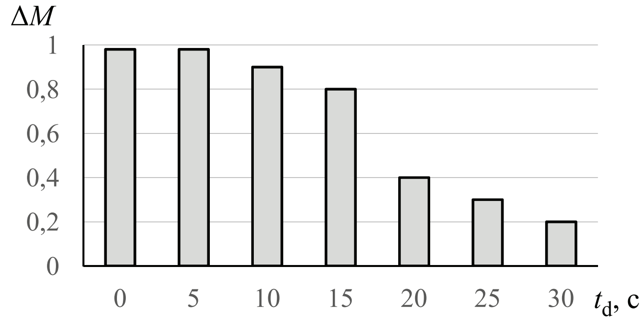
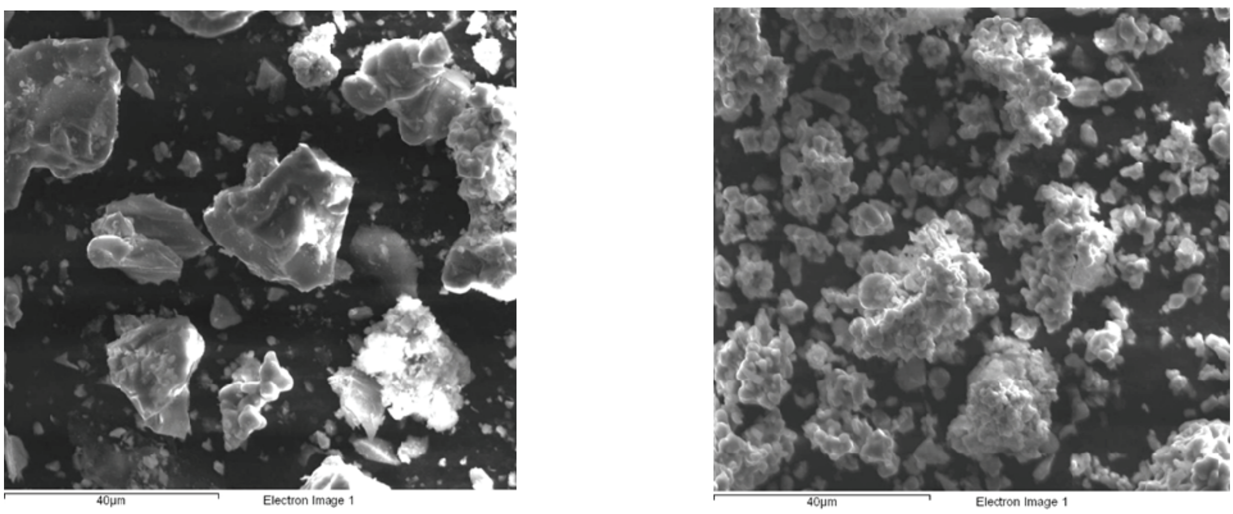


Fig. 6. The dependence of the crushed mass of products on the delay time before the application of mechanical treatment

The obtained dependence can be explained as follows. Under optimal conditions, the course of post-processes (sintering, compacting, cooling) must provide a minimum strength allowing the crushing of the material. If the delay time t_d is increased, or mechanical treatment is not applied, the material may acquire such strength that its subsequent crushing will be challenging. Thus, one of the key issues of the SHS process in terms of mechanical treatment is the choice of the optimal time delay, which, other factors being equal, will deliver more complete phase formation and the maximum yield of the crushed powder.

Fig. 7 shows the morphology of the synthesized powder. Mechanical treatment acts as a kinetic factor, influencing the structure formation, the change of grain size and morphology. Applying a shear load to immature material, it is possible to influence the morphology of the obtained powder.



a) *b*)

Fig. 7. The morphology of the synthesized powder:
a – without mechanical treatment; *b* – with mechanical treatment

After SHS the obtained agglomerated particles are fragmentized. Mechanical treatment provides for a more rounded shape of the synthesized material.

Conclusion

It is established that when a mechanical treatment is applied to the synthesized material, its phase formation presents a more complete process, compared with the material obtained by SHS without mechanical treatment. The highest content of the main phase – $MoSi_2$ (87 %) is contained in the material subjected to mechanical treatment with the delay time of 10 seconds.

It is shown that after SHS without mechanical treatment and time delays of over 30 s the synthesized material consists mainly of agglomerated particles fused with each other. The crushed mass of molybdenum disilicide is not more than 20 %. Mechanical treatment of SHS products leads to almost 100 % output of powder of a fineness of less than 500 microns.

Mechanical treatment results in the mixing of the emerging fine structure and inhibits crystallization and recrystallization. Applying a shear load to immature material, it is possible to influence the morphology of the obtained powder.

Acknowledgment

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