The study of pressing mechanically activated niobium and silicon powder mixtures

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Abstract. The paper presents the results obtained in the study of the pressing process of mechanically activated powder mixtures of the niobium – silicon system. Pressing often precedes the process of self-propagating high-temperature synthesis and the initial density of the compressed samples can have a significant impact on the regime of subsequent high-temperature combustion, on the composition and properties of the final product (niobium silicide). The obtained dependences of porosity on the time of mechanical activation showed the features of pressing, which are associated with the formation of layered agglomerates in the process of mechanical activation. It was found that the compression curves of mechanoactivated powders differ qualitatively from the standard compression curves of fine powders. The paper considers the influence of mechanical activation time on the density of the compressed samples obtained by varying the pressing pressure and the time spent under the press. The relationship between the density of compresses and layered agglomerates, which are formed during mechanical activation, is considered.

1. Introduction

Pressing is the compression of metal powder in the mold under pressure. During deformation, the initial volume of powder decreases, and a compact with a specified shape, size and properties is formed. The change in the initial volume is caused by the displacement and deformation of individual particles which, in turn, fill the voids formed when powder is placed in the mold. For brittle materials, deformation is manifested in the destruction and fragmentation of asperities on the surface of particles [1].

Pressing is a preliminary stage of self-propagating high-temperature synthesis. In some cases, the combustion mode and the composition of final products depend on the porosity of compacts.

The idealized curve of powder compression should have three characteristic sections (Figure 1). The packing density of the particles rapidly increases at the first stage (section A), when the particles move relatively freely, occupying voids. Finally, the particles are packed as tightly as possible and a horizontal section B appears. The resistance of the particles to compression is high and, despite the increase in pressure, the volume of powder does not decrease for some time, since the particles do not move and experience only elastic strain. When the pressure exceeds the compression resistance of the powder, the plastic strain of the particles takes place (section C). The more plasticity of the metal, the lower the compaction pressure due to the deformation of the particles. For brittle materials which do not experience plastic strain, the third stage is impossible, and with increasing pressure, the particles
are destroyed. In practice, during the pressing process, the above-mentioned compaction stages take place almost simultaneously: deformation of some particles occurs at low pressures, while individual particles continue to move under considerable loads.

At present, silicides are used in various fields of science and engineering for special production processes or creation of products with special properties. Silicides of refractory metals are currently widely used due to such properties as: high heat resistance, thermal resistance, preservation of mechanical characteristics in a wide temperature range, high conductivity. In recent years, a lot of studies have been conducted to find new refractory materials. The most promising materials are intermetallides and intermetallide based-composites in the form of eutectics, for example, niobium matrix strengthened by niobium silicide intermetallides. Some parts made from this composite can operate for a long time at temperatures about 200 °C higher than the operation temperatures of similar parts. In recent years, active studies have been also conducted to obtain niobium-silicon compounds in various ways and investigate microstructures and mechanical properties [2, 3, 4, 5, 6, 7].

The niobium-silicon system is low-energy and SHS cannot be conducted without preliminary preparation. Often, such preparation is mechanical activation (MA). Studies of the effect of preliminary MA on SHS processes attract much attention [8,9,10,11,12,13,14]. MA is a process in which many simultaneous and opposite phenomena occur. This is the grinding of powder mixtures and formation of layered agglomerates, increasing the contact surface of initial dissimilar components and formation of the products of their interaction. In this regard, the characteristics of a mixture subjected to MA are very different as compared to those of ordinary powder mixtures. The changes in a powder mixture subjected to MA affect all further technological operations, including pressing. In some cases, the SHS mode, the composition, structure and properties of final products depend on the porosity of compacts. Pressing has a strong effect on the crystal structure and may lead to its changes [15, 16, 17, 18, 19]. Therefore, studying different powder mixtures subjected to pressing and criteria characterizing the compressibility of different metal powders is of scientific and practical interest [20].

The aim of the work was to carry out joint mechanical activation of a powder mixture of niobium and silicon at different MA times, to compress samples by varying the pressing pressure and the time of the sample under the press, to calculate the resulting sample density and to find the dependence of the density on the MA time.

The object of this study is the behavior of the powder mixture during compression and compaction. The subject of research is the pressing process.

In this paper, we will describe and discuss the dependence of the porosity of pressed samples on the pressing pressure for different durations of exposure under the press after different times of mechanical activation of the niobium-silicon powder mixture. The paper is structured as follows: part 2 describes the conditions for conducting MA experiments and shows the calculation of the initial

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**Figure 1.** Idealized curve of powder compression.
porosity of pressed samples. Section 3 is devoted to the analysis of graphical dependences of the porosity of samples on the pressing pressure, on different exposure times under the press, and on different MA times. Changes in bulk density and specific surface area vs MA time are shown graphically. Microphotos of powder mixtures after different MA time, analysis and discussion of the obtained data are also given in this section. Section 4 presents the conclusions obtained from the results of the study.

2. Experiment

In experiments, a planetary energy-intensive centrifugal mill (1450 rotations per minute) with water-cooled drums was used for MA. The walls of the drums and the balls 5 mm in diameter were lined with ground material to eliminate iron. The ball to powder weight ratio was 20:1 in all experiments. The weight of the powders was 30 g. A mixture of initial components was placed in the drums of the planetary mill, and the time of MA ranged from 0.25 min to 120 min in argon with a purity of 99.99%. After MA, the powder mixture was pressed into cylindrical samples with a diameter of 10 mm in a steel mold. Pressing was conducted on a hydraulic press at a pressure from 4.0 to 16.0 MPa, and the pressing time under maximum load was also varied from 0.25 to 2 min.

The experimental studies of pressing mechanically activated powder mixtures showed that the porosity of the pressed sample depended on the MA time. In the studies the composition was used as follows: Nb - 62.3 wt.%, Si - 37.7 wt.%. For uniform pressing, the mass of the powder mixture was selected in such a way that after pressing the sample height was also 10 mm.

The initial porosity of pressed samples was determined by the formulas: [1]

\[ \eta_o = \frac{d_k - d_n}{d_k} \cdot 100\%, \]  

\[ d_k = \frac{d_A d_B M_A + M_B d_A}{M_A d_B + M_B d_A}, \]  

\[ d_n = \frac{m}{V}, \]

where \( \eta_o \) is the initial porosity of the sample, %,  
\( d_k \) is the density of the compact, g/cm\(^3\),  
\( d_n \) is the density of the pressed material, g/cm\(^3\),  
\( m \) is the mass of the sample, g,  
\( V \) is the volume of the sample, cm\(^3\),  
\( d_A \) is the density of component A, g/cm\(^3\),  
\( d_B \) is the density of component B, g/cm\(^3\),  
\( M_A \) is the mass concentration of component A in the mixture, %,  
\( M_B \) is the mass concentration of component B in the mixture, %,  
\( M \) is total mass, g.

The structure of activated powder mixtures and combustion products were studied by scanning electron microscopy (Philips SEM515).

3. Results

Figures 2 - 6 show the porosity of the pressed sample as a function of the pressing pressure and time at the maximum pressure under pressing for different MA times.
It can be seen that these dependences are very different from the idealized curve of powder compression. MA powders behave differently under pressing than untreated powders. Figure 2 shows porosity as a function of pressure during pressing the samples after 2 min MA. For all pressing times, with a pressure of 11 MPa, porosity significantly increases. This is explained by a change in morphology of the powder mixture after this MA time. Increasing the pressing pressure up to 11 MPa leads to the decrease in porosity, and the mixture is compressed due to the movement of particles and agglomerates relative to each other.

The fragmentation of agglomerates takes place upon reaching a pressure of 11 MPa, and the volume increases due to different defects, cracks and fragments of the agglomerates. Such an increase in volume due to elastic and inelastic changes at the stress above the elastic limit is known as a dilatancy phenomenon. After 2 min MA, the agglomerates formed are still loose and easily broken under pressing. With longer MA times, the agglomerates become denser and smaller, and the increase in porosity with increasing pressing pressure is not so pronounced for the long MA time. The images of the mixture and layered agglomerates are presented in Figure 7. It can be seen that after 5 min MA the powder mixture represents large agglomerates surrounded with smaller ones. Initial silicon is larger than niobium, therefore such agglomerates are residual silicon surrounded with more plastic niobium. With the longer MA time, the size of the formed layered agglomerates decreases (Fig. 7 b).

Figure 2 - Porosity ($\eta$) of the pressed samples as a function of pressure during pressing (P) after 2 min MA. (a) pressing time is 0.25 min, (b) pressing time is 1 min, (c) pressing time is 2 min.

Figure 3 - Porosity ($\eta$) of the pressed samples as a function of the pressing pressure (P) after 5 min MA. (1) pressing time is 0.25 min, (2) pressing time is 1 min.

Figure 4 - Porosity ($\eta$) of the pressed samples as a function of the pressing pressure (P) after 15 min MA. (1) pressing time is 0.25 min, (2) pressing time is 1 min, (3) pressing time is 2 min.
Figure 5 - Porosity (η) of the pressed samples as a function of the pressing pressure (P) after 60 min MA. (1) pressing time is 0.25 min, (2) pressing time is 1 min, (3) pressing time is 2 min.

Figure 6 - Porosity (η) of the pressed samples as a function of the pressing pressure (P) after 120 mins MA. (1) pressing time is 0.25 min, (2) pressing time is 1 min, (3) pressing time is 2 min.

Figure 7. Micrographs of powder mixtures after 5 min MA (a) and 60 min MA (b)

The porosity of the pressed sample as a function of MA time at the different press load and the pressing time is given in Figs. 8, 9, 10. Regardless of the pressing time (0.25, 1, 2 min) and the applied pressure (6.0; 8.0; 11.0; 15.0 MPa) the curves are qualitatively similar. Porosity increases in the range of MA time from 1 to 5 minutes, reduces in the range of MA time from 5 to 15 minutes and then slowly decreases with a further increase in the time of mechanical activation.

Bulk density as a function of MA time was studied (Figure 11). It is known that the powder with larger particles has a higher bulk density and compressibility than the same powder with smaller particles [3]. During MA, the initial components are ground and new active surfaces are created, forming silicide at their contact points. These processes take place during MA, but different processes predominate at different times. At the initial stage of the process, the grinding of powders takes place and the particles are not capable of sticking together into large dense agglomerates. The particles and the agglomerates formed have the same size. The powder mixture with particles of approximately the same size will be less compressible than that with particles of different size. Powders that are capable, due to their size, of filling voids formed during the packing of large particles will be more compressible under equal conditions than monodisperse powders. Therefore, porosity decreases after
longer MA, when large agglomerates and small fragmentation particles are formed. In addition, during long MA a larger amount of silicides is formed, which hold the agglomerates together, not allowing them to be broken under pressing. The change in MA time leads to the change in the specific surface of the powder mixture. These changes are plotted in Figure 12. An increase in specific surface indicates not only a decrease in particle size, but also an increase in "roughness" on the surface of particles. The presence of a developed defective and rough surface blocks the movement of particles relative to each other during pressing. With long MA the agglomerates are packed and in the study of the specific surface by the BET method, argon cannot penetrate into all defects and cracks, as with short MA times, and the specific surface values obtained are low. The increase in the specific surface occurs for two min MA, then these values decrease and remain at approximately the same level.

Figure 8 - Porosity ($\eta$) of pressed samples as a function of MA time $\tau$ at a pressing time of 0.25 min; (1) pressing pressure ($P$) = 6.0 MPa, (2) $P$ = 8.0 MPa, (3) $P$ = 11.0 MPa, (4) $P$ = 15.0 MPa

Figure 9 - Porosity ($\eta$) of pressed samples as a function of MA time $\tau$ at a pressing time of 1 min; (1) pressing pressure ($P$) = 6.0 MPa, (2) $P$ = 8.0 MPa, (3) $P$ = 11.0 MPa, (4) $P$ = 15.0 MPa

Figure 10 - Porosity ($\eta$) of pressed samples as a function of MA time $\tau$ at a pressing time of 120 s; (1) pressing pressure ($P$) = 6.0 MPa, (2) $P$ = 8.0 MPa, (3) $P$ = 11.0 MPa, (4) $P$ = 15.0 MPa
4. Conclusion
The study of pressing mechanically activated powder mixtures showed how the morphology of the powder mixture subjected to MA affected the pressing and clarified the processes occurring during mechanical activation for different times. After 2 min MA, the initial powders are ground with the formation of agglomerates which consist of similar small agglomerates, mechanosynthesized silicides and initial particles not strongly bonded to each other. Agglomerates are loose and rough formations; therefore, they cannot move freely relative to each other at low pressing pressures and can break at high pressures. After 5 min or more mechanical activation, layered agglomerates become denser and harder. Therefore, they are easily compressed and are not broken as intensively as agglomerates after 2 min activation under equal pressing conditions.

Appendices
SHS - self– propagating high-temperature synthesis,
MA - mechanical activation
SEM - Scanning Electron Microscope

References
[1] Libenson G A Fundamentals of Powder Metallurgy 1987 (Moscow: Metallurgy) p. 208
[2] Rende M U, Zaoyu S U, Guanghong H U, 2016 Journal of Aeronautical Materials 36(2) 1 doi 10.1186/s1005-5053.2016.2.001
[3] Yin W X, Guo Y Q, 2017 Materials & Design 116 461 doi.org/10.1016/j.matdes.2016.12.033
[4] Ning X Y, Xu J M, 2015 Materials Science in Semiconductor Processing 30 636 doi.org/10.1016/j.mssp.2014.09.030
[5] Yueling G L, Bin K S, Zhang J S, et al 2017 Journal of Alloys and Compounds 696 516 doi.org/10.1016/j.jallcom.2016.11.236
[6] Sankar M, Phanikum G, SatyaPrasada V.V. 2016 Materials Today: Proceedings 3(9) 3094 doi.org/10.1016/j.matpr.2016.09.025
[7] Shkoda O A, 2016 Inorg. Mater. Appl. Res. 7 429 doi.org/10.1134/S2075113316030187
[8] Shkoda O A, Terekhova O G, 2016 Int. J Self-Propag. High-Temp. Synth. 25 14. doi.org/10.3103/S106138621601012X
[9] Shkoda O A, 2018 *Int. J Self-Propag. High-Temp. Synth.* **27** 60. doi.org/10.3103/S1061386218010089
[10] Shkoda O A, Lapshin O V, 2016 *Russ Phys J* **59** 1231 doi.org/10.1007/s11182-016-0896-3
[11] Seplyarskii B S, Kochetov N A, Kochetkov R A, 2016 *Combust Explos Shock Waves* **52** 307. doi.org/10.1134/S0010508216030084
[12] Korchagin M A, Gavrilov A I, Bokhonov B B, et al. 2018 *Combust Explos Shock Waves* **54** 424. doi.org/10.1134/S0010508218040068
[13] Boldyrev V V, 2018 *Her. Russ. Acad. Sci.* **88** 142 doi.org/10.1134/S1019331618020016
[14] Mansurov Z A, Mofa N N, Sadykov B S, et al. 2016 *Int. J Self-Propag. High-Temp. Synth.* **25** 166 doi.org/10.3103/S1061386216030080
[15] Boldyreva E V, 2004 *Russ. Chem. Bull.,* **53** (7) 1351 doi.org/10.1023/B:RUCB.0000046233.96144.29
[16] Fedotov A P, Shakhtshneider T P, Chesalov Y A et al. 2009 *Pharm Chem J* **43** 68. doi.org/10.1007/s11094-009-0225-z
[17] Wang X U, Zak Z F, 2015 *Journal of Refractory Metals and Hard Materials* **53** 134 dx.doi.org/10.1016/j.jirmhm
[18] Francine A C, Gilberto M, Uilame U G, et al 2015 *Int. Journal of Refractory Metals and Hard Materials* **51** 207 doi.org/10.1016/j.jirmhm
[19] Jun-Ill Song, Geon-Yong Lee, Joon-Phil Choi, et al 2018 *Powder Technology* **338** 333 doi.org/10.1016/j.powtec.2018.06.041
[20] Ludovit P, Dudrova E, Bidulsky R, et al 2017 *Powder Technology* **322** 447 doi.org/10.1016/j.powtec.2017.09.027