Physical and mechanical properties of composite materials in the MoSi$_2$-SiC-TiB$_2$ system

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Abstract. In this work, we obtained ceramic materials based on MoSi$_2$, hardened by SiC and TiB$_2$ particles, which makes it possible to increase the heat resistance of the composite and increase the level of its physical and mechanical properties (at a relative density of more than 99.0 %, tensile strength in bending $520 \pm 10$ MPa). The shrinkage, density, porosity and weight loss of composite materials during sintering were studied. The value of the ultimate strength in bending of materials at the optimum sintering temperature is determined. The maximum values of physical and mechanical properties are achieved for a material composition of $50.0$ vol. % MoSi$_2$ + $15.0$ vol. % SiC + $35.0$ vol. % TiB$_2$: $E = 471 \pm 10$ GPa; $\sigma_b = 520 \pm 10$ MPa; $K_{IC} = 4.4 \pm 0.1$ MPa$\cdot$m$^{1/2}$; $HV = 22.1 \pm 0.1$ GPa obtained at a sintering temperature of 1950 °C.

1. Introduction
Materials based on molybdenum disilicide retain stability and workability in an oxidizing environment at temperatures up to 1750 °C. Such materials are the main components of heaters, artillery gun liners, lining of the combustion chambers of jet engines, protective caps of high-speed flying vehicles, etc. [1, 2].

To solve modern production problems, it is often necessary to increase the level of mechanical properties of materials based on MoSi$_2$; for this, reinforcing components are introduced into the material - SiC$_w$, Si$_3$N$_4w$ whiskers and SiC$_f$ fibers, etc. [3, 4].

In [5], a method was proposed for hardening molybdenum disilicide by co-mixing the powder components of MoSi$_2$ with SiC particles, followed by hot pressing. Composite materials based on silicon carbide are known, containing silicon, MoSi$_2$ and Si, NbSi$_2$ and Si, which are synthesized during the impregnation of a chemically active melt [6].

A significant amount of work has been devoted to studies of the MoSi$_2$–SiC system; however, the possibilities of obtaining such ceramics by free sintering and the study of its mechanical properties have hardly been studied.

In [7–9], it was noted that materials of the MoSi$_2$–SiC–TiB$_2$(ZrB$_2$) system can be promising composite ceramics based on molybdenum disilicide. It was previously shown that SiC coexists with a large number of refractory compounds, among which carbides (TiC, ZrC, HfC, NbC, TaC) and borides (TiB$_2$, ZrB$_2$, HfB$_2$) of transition metals should be distinguished. Of greatest interest are the SiC – TiB$_2$ and SiC–ZrB$_2$ systems [10–13]. There is no information on the three-component state diagram of the MoSi$_2$–SiC–TiB$_2$ system; therefore, it is very promising to study the properties of both the two-component MoSi$_2$–SiC system and the system as a whole.
The aim of the work is the sintering of dense ceramic materials based on MoSi$_2$ by solid-phase sintering with the addition of reinforcing particles of SiC and TiB$_2$, the study of the structure and mechanical properties of the obtained composites.

2. Materials and Method
To obtain sintered composite materials of the MoSi$_2$–SiC, MoSi$_2$–SiC–TiB$_2$ systems, the following powders were used as initial components: MoSi$_2$, particle size $d_{0.5} = 6.5 \mu$m; SiC, particle size $d_{0.5} = 0.8 \mu$m; TiB$_2$, particle size $d_{0.5} = 14.3 \mu$m. MoSi$_2$ and TiB$_2$ powders were additionally ground in a VML-1,5 vibration mill in isopropyl alcohol for 60 hours. The particle size of the powders after grinding was: MoSi$_2$ - $d_{0.5} = 0.85 \mu$m; TiB$_2$ - $d_{0.5} = 0.78 \mu$m.

The materials were prepared using standard ceramic technology [14–16], including mixing powders in a drum mixer in a gaso-line environment with the simultaneous introduction of a temporary technological binder — 4 % wt. Paraffin. Over 100 % of charge components, molding of sample blanks measuring 6×6×50 mm and ø25×8 mm on a hydraulic press at a pressure of 100 MPa. The samples were dried at a temperature of 120 °C for 3 h. and sintered in a vacuum oven at temperatures of 1800, 1850, 1900, and 1950 °C, in an Ar atmosphere, for 1 h. Shrinkage of materials was determined on a DIL 402c dilatometer. The compositions of the samples are presented in table. 1.

| №   | Content of components, vol. % | Theoretical density $\rho_{\text{theor.}}, \text{g/cm}^3$ |
|-----|-------------------------------|--------------------------------------------------|
| 1   | MoSi$_2$ 75 SiC 25 TiB$_2$     | 5.50                                             |
| 2   | 60 40 -                                                       |
| 3   | 80 10 10                                                     |
| 4   | 33.4 33.3 33.3                                  4.90                             |
| 5   | 50 15 35                                             5.26                             |
| 6   | 50 25 25                                             5.37                             |

The particle size of the powders was determined using a Malvern Mastersizer 3000 laser dispersion analyzer. The density of the samples was determined by hydrostatic weighing. Porosity was measured using a Meiji Techno IM 7200 optical microscope and a Thixomet computer image analyzer. The elastic modulus was determined, using the excitation of resonant vibrations, on the ZVUK-130 unit. Strength in three-point bending was measured on a Shimadzu AG-300KNX unit. The hardness and coefficient of fracture toughness were determined by introducing the Vickers pyramid into the material and measuring the size of the diagonals of the indent and the cracks emanating from it on a TP-TR-1 macrohardness tester with a load of 2 kg. The microstructure was examined using a Meiji Techno IM 7200 optical microscope. The equipment was provided by the Engineering Center of St. Petersburg State Technological Institute.

3. Results and discussion
The optimal temperature of solid-phase sintering of materials was determined by analyzing the shrinkage curves by heating the samples to a temperature of 1900 °C in an Ar media (this temperature is lower than the eutectic). Previously, in [17], it was shown that the minimum temperature of the liquid phase formation (eutectic temperature) in the MoSi$_2$–SiC system is 1900 °C with a component ratio of 70 % vol. MoSi$_2$ + 30 % vol. SiC. The results of the shrinkage of the samples are presented in table. 2.

Shrinkage increases when a third component is introduced into the material. Maximum shrinkage is observed for materials of compositions 3–6 containing titanium diboride. The addition of TiB$_2$ and its uniform distribution in the material leads to the formation of a rigid refractory skeleton of SiC and TiB$_2$ particles, and molybdenum disilicide, as the least refractory component (T = 2030 °C) upon contact melting with SiC and TiB$_2$, acts as a source of the liquid phase that activates the process compaction of
materials (table 2). When more refractory components (SiC - \( T = 2730 \, ^\circ C \) and TiB\(_2\) - \( T = 3230 \, ^\circ C \)) are introduced into the material based on MoSi\(_2\), the temperature to reach maximum shrinkage increases. The maximum shrinkage of 17.2 and 18.4 \% is observed for materials of compositions 4 and 5 at a temperature of 1900 °C (Table 2).

| №  | Shrinkage \( \gamma \) (at \( T_{sintering} \), °C), % | Density \( \rho_{rel} \) (at \( T_{sintering} \), °C), % | Porosity \( \Pi \) (at \( T_{sintering} \), °C), % | Mass loss \( \Delta \)m (at \( T_{sintering} \), °C), % |
|----|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1  | 8.8 (1800)                                   | 96.8 (1850)                                   | 3.1 (1850)                                   | 0.4 (1900)                                   |
| 2  | 9.8 (1880)                                   | 97.4 (1900)                                   | 2.5 (1900)                                   | 0.5 (1950)                                   |
| 3  | 12.5 (1820)                                  | 98.1 (1850)                                   | 2.0 (1850)                                   | 0.5 (1900)                                   |
| 4  | 17.2 (1900)                                  | 99.0 (1950)                                   | 1.0 (1950)                                   | 0.3 (1950)                                   |
| 5  | 18.4 (1900)                                  | 99.3 (1950)                                   | 0.8 (1950)                                   | 0.3 (1950)                                   |
| 6  | 16.8 (1890)                                  | 99.0 (1900)                                   | 0.9 (1900)                                   | 0.5 (1950)                                   |

The table 2 shows the values of density and porosity of sintered materials at the optimum temperature for each composition. Samples sintered at a temperature close to the temperature of maximum shrinkage do not reach the highest compaction, which is most likely due to the need for a slight overheating of the system. However, with significant overheating (more than 50 °C), increased porosity is observed, which is associated with the evaporation of oxides at temperatures above 1900°C (Table 2), present a thin layer on the starting particles, and at a higher temperature, loss of silicon by disilicide with the transition to Mo\(_5\)Si\(_3\).

The elastic modulus of materials is affected by the presence of defects (microcracks, pores, etc.). Since the transition metal borides are characterized by a large value of the elastic modulus, with an increase in the TiB\(_2\) content in the composition of the material, \( E \) increases (table 3) due to the approximation of the density of the material to the theoretical. The values of the elastic modulus of compositions 1 and 2 depend on the quality of the obtained samples. For example, hot-pressed materials are characterized by \( E \) values close to theoretical.

An important characteristic of composite materials is crack resistance, which also depends on the density and structural defects (porosity) in the material. When moving from a two- to three-component system, it is possible to obtain a finer-grained structure of materials, since each additional component of the system is an inhibitor of grain growth of single- and two-phase materials, which reduces mass transfer and grain recrystallization during sintering. Therefore, compositions 3–6 are characterized by increased density (Table 2) and, as a consequence, higher levels of crack resistance coefficients (Table 3) and bending strength (Figure 1). The maximum value of the coefficient of crack resistance \((4.4 \pm 0.1 \, \text{MPa} \cdot \text{m}^{1/2})\) was achieved on a material with an equivalent volume content of components – 33,4 vol. % MoSi\(_2\) + 33,3 vol. % SiC + 33,3 vol. % TiB\(_2\).
The hardness of materials is defined as the additive value between the hardnesses of the phases contained in it, therefore, at a high titanium diboride content \( H_T = 33.7 \text{ GPa} \), the value of the HV composite increases. Cracks in the material propagate mainly by the intercrystalline mechanism, rounding grains, which, when using three-component systems, leads to an increase in the crack path and, as a result, to an increase in the coefficient of crack resistance (Table 3). An exception may be materials with a high content of molybdenum disilicide (compositions 1 and 3) having low hardness (Table 3), such materials are partially destroyed in accordance with the transcry stalline fracture mechanism [18, 19].

Strength properties of sintered materials as well as elastic characteristics depend on the density determined by the optimal technological sintering conditions. High bending strength is achieved on materials of compositions 4–6 (Fig. 1) at a temperature that ensures partial melting of the components (based on MoSi2) and, at the same time, their little evaporation. For compositions 4 and 5, most likely, with increasing temperature (more than 1950 °C), a sharp decrease in strength is observed, which is associated with the possible evaporation of silicon formed during partial metallization of the chemical bond in MoSi2 with its conversion to Mo5Si3 and the liquid phase entering the material surface with the formation of pores in the volume of the material.

Figure 2 shows the microstructures of composite materials of the MoSi2–SiC and MoSi2–SiC–TiB2 systems, where the light gray phase is MoSi2, the dark phase is SiC, and the dark gray phase is TiB2.
The high mechanical properties of the composite materials of the MoSi$_2$–SiC and MoSi$_2$–SiC–TiB$_2$ systems are ensured by the correct choice of sintering temperature, the use of fine powders and uniform distribution of the starting components over the volume of the material.

4. Conclusion
The microstructure was studied and the mechanical properties of composite materials of the MoSi$_2$–SiC and MoSi$_2$–SiC–TiB$_2$ systems obtained by solid phase sintering were studied. The effect of introducing the third component on the mechanical properties of ceramics is shown. When titanium diboride is introduced into the material, its modulus of elasticity, coefficient of crack resistance, and hardness increase. The bending strength of materials is determined by the selected mode of sintering of ceramics. The maximum values of mechanical properties are achieved on a material with a composition of 50.0 vol. % MoSi$_2$ + 15.0 vol. % SiC + 35.0 vol. % TiB$_2$: $E = 471 \pm 10$ GPa; $\sigma_b = 520 \pm 10$ MPa, $K_{IC} = 4.4 \pm 0.1$ MPa · m$^{1/2}$; $HV = 22.1 \pm 0.1$ GPa at a sintering temperature of 1950 °C.

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