Features of the synthesis and consolidation of MeIVB2–(MeIV, Mo)Si2 ceramic powder for high-temperature applications

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Abstract. ZrB2–ZrSi2–MoSi2 and HfB2–HfSi2–MoSi2 composite ceramic powders were obtained by magnesiothermic SHS. The synthesized powders were consolidated by hot pressing in the temperature range of 1200–1250°C at 30 MPa. The structure and phase composition of the powders and compact ceramics were studied by X-ray powder diffraction analysis and scanning electron microscopy. ZrB2/HfB2, ZrSi2/HfSi2, ZrSi, and MoSi2 were the key phases of the ceramic powders and sintered ceramics. The average grain size of the powders after grinding was 6–8 µm. Saturation of the ZrSi phase with silicon and increased ZrSi2 content were observed during hot pressing. The dense ceramics had a residual porosity of 1.1–7.4%, which was largely dependent on the contents of silicides in SHS powders.

1. Introduction
Designing novel structural materials to fabricate various thermally loaded components of modern high-speed aircrafts is the primary objective of materials science. These materials are supposed to ensure constant geometry and size; stable chemical, physical and mechanical properties, as well as the heat-shielding performance of the product throughout its entire lifecycle [1]. The use of these structural materials is expected to improve the reliability and durability of thermally loaded structures, to enhance the performance of propulsion systems, and to reduce the levels of harmful emissions by increasing the temperature of combustion gases. From this perspective, the high-temperature ceramics based on HfB2 and ZrB2 borides shows great promise as the melting point (> 3000°C) and high thermal conductivity of these borides are comparable to those of a number of metal-based materials [2]. Furthermore, this ceramics is characterized by an elevated ablation resistance as compared to the conventionally used SiC-based materials [3, 4]. However, despite all the benefits, pure boride ceramics are not applied in practice, since low ductility of this material makes it poorly compactible and sinterable. Furthermore, its resistance to high-temperature oxidation is limited to temperatures as low as 1100°C [6] because of the formation of the B2O3 glassy phase (T_melt = 480°C), which is converted to a volatile B2O3 oxide at temperatures above 1100°C [7].

TaSi2, ZrSi2 or MoSi2 silicides are added to the composition of boride ceramics to enhance its high-temperature stability and strength [8]. Oxidation of these silicides gives rise to oxide films of different compositions. Oxidation of MoSi2 leads to formation of a SiO2 protective layer on the surface,
ensuring protection at temperatures up to 1800°C [9, 10]. Oxidation of ZrSi2 yields the ZrSiO4/SiO2 glassy phase, which efficiently impedes diffusion of oxygen into the bulk of the ceramic material due to its barrier properties. Boron present within the ceramics gives rise to the SiO2–B2O3 borosilicate glass that can self-heal the imperfections, which are inevitably formed during high-temperature oxidation [11].

Hot pressing (HP) and spark plasma sintering (SPS), as well as the hybrid technologies (reaction HP and SPS), are the methods conventionally used to fabricate the consolidated boride-silicide ceramics [12, 13]. However, their application is associated with a number of technological challenges: for example, there is a significant difference in the melting points of the initial components, the powdered raw material has to be of high purity, etc. Self-propagating high-temperature synthesis (SHS) is an alternative technique [14, 15]. The technology of forced SHS compaction allows one to produce the boride-silicide ceramics with fine-grained structure and porosity of ~ 1.5–3.0% [16]. It is reasonable to use the combined method involving two stages—fabrication of a heterophase powder by SHS and its subsequent consolidation by HP or SPS—to manufacture nonporous ceramics with the retained disperse structure. It is promising to use magnesiothermic SHS, a rather energy-efficient technology, to produce heterophase powders based on refractory compounds [15]. This technology employs heat released during the course of chemical reactions in the combustion mode. This technology is economically sound as the cheaper oxide raw material can be used.

This study focuses on the potential of conducting magnesiothermic synthesis of heterophase MeIVB2−(MeIV, MeVI)Si2 ceramic powders (MeIV = Hf, Zr and MeVI = Mo) in a broad range of concentrations of the initial components followed by consolidation of the resulting powders by hot pressing.

2. Experimental

The MeIVB2−(MeIV, MeVI)Si2 ceramic powder was produced by magnesiothermic reduction of hafnium oxide HfO2, silicon oxide SiO2, molybdenum oxide MoO3 (all these substances being of pure for analysis grade) and boron oxide B2O3; the content of the main substance in these powders was ≥ 98.0%. B2O3 powder with the grain size of 1–2 mm was ground in a planetary ball mill (PBM) at a 1:5 ratio until the fraction with grain size < 100 µm was obtained. Magnesium powder of MPF-3 grade (98.5–99.5%) with the average grain size of 100–150 µm was used as a reducing agent.

The initial components were pre-blended in the PBM at a 1:6 ratio between the hard-alloy grinding balls and powders. The resulting loose mixtures were subjected to SHS in an 8 L universal SHS-8 setup in argon environment under an excess pressure of 3 MPa. The combustion reaction was initiated using a tungsten filament coil and monitored using a gauge detecting pressure inside the reaction chamber. A general scheme of magnesiothermic synthesis of ceramic powders is described by formula (1):

\[
(x + z)2\text{SiO}_2 + (x + y)(\text{ZrO}_2/\text{HfO}_2) + z\text{MoO}_3 + y\text{B}_2\text{O}_3 + w\text{Mg} \rightarrow (x + z)2\text{Si} + (x + y)(\text{Zr/Hf}) + z\text{Mo} + y2\text{B} + w\text{MgO} + Q \rightarrow x(\text{ZrSi}_2/\text{HfSi}_2) + y(\text{ZrB}_2/\text{HfB}_2) + z\text{MoSi}_2 + w\text{MgO} + Q
\]

where \(x, y, z,\) and \(w\) are the coefficients depending on the given composition of the final product; \(Q\) is the quantity of heat released during the chemical reactions, J/mol.

Once synthesis had been completed, the resulting sinter cake was crushed and disintegrated until the grain size of the resulting powder was < 250 µm. The target product based on hafnium and molybdenum borides and silicides was separated from magnesiothermic oxide and unreacted magnesium by chemical enrichment in an aqueous solution of hydrochloric acid of chemically pure grade. Acid-soluble magnesium salts were removed by filtering off the resulting precipitate of the target product, washing it with water, and drying at 100°C. The yield of the target product (\(\eta\)) was calculated using formula (2):

\[
\eta = \frac{(m/M) \times 100}{\text{weight of the semi-finished product}}
\]

where \(m\) is the weight after the enrichment and \(M\) is the weight of the semi-finished product.

To ensure particle deagglomeration, the resulting powder was ground in a PBL and an MPP-1 planetary centrifugal mill (PCM).
The adiabatic flame temperature \( T_{ad} \) of the reaction mixtures was computed using the THERMO software (Merzhanov Institute of Structural Macrokinetics and Materials Science, Russia); the mass burning rate was calculated using formula (3):

\[
U_b^m = \frac{G}{\tau} \quad \text{g/s}
\]  

where \( U_b^m \) is the mass burning rate (g/s); \( G \) is the weight of the reaction mixture loaded into a graphite container; \( \tau \) is the combustion time that is defined as a section between the point where pressure in the reaction chamber starts to rise and the point where it starts to decrease.

The phase analysis of the ceramic and hot-pressed powders was carried out on a DRON-4 diffractometer (AO "Burevestnik Research and Production Enterprise", Russia) using Cu K\( \alpha \) monochromatic radiation. The XRD patterns were interpreted using the JCPDS database. The microstructure and morphology of the ceramic powders and hot-pressed samples were studied using an S-3400N scanning electron microscope (Hitachi High-Technology Corporation, Japan) equipped with a NORAN System 7 X-ray energy-dispersive spectrometer (Thermo Scientific, USA) to determine the elemental composition of the structural components. SEM images were recorded in two modes (secondary and backscattered electron imaging, magnifications of \( \times100–5000 \)). The granulometric compositions of SHS powders were identified on an ANALYSETTE 22 MicroTec Plus laser particle sizer (Dr. Fritsch, Germany). Hot pressing of the ceramic powders was conducted using a Direct Hot Pressing-DSP-515 SA machine (Dr. Fritsch Sondermaschinen GmbH, Germany) in a graphite die mold 50 mm in diameter at the compaction temperature of 1200–1250°C and a pressure of 30 MPa.

Table 1. Compositions of the initial mixtures, combustion parameters, and yield of the target product

| Composition no. | Content of the initial components in the green mixture, wt % | \( T_{ad} \), K | \( U_b^m \), g/s | \( \eta \), % |
|----------------|------------------------------------------------------------|--------------|----------------|---------|
| ZMSB-1         | SiO\(_2\) 16.2, ZrO\(_2\) 29.9, HfO\(_2\) - , MoO\(_3\) 5.5, B\(_2\)O\(_3\) 10.3, Mg 38.1 | 2120         | 9.4            | 34      |
| ZMSB-2         | SiO\(_2\) 23.0, ZrO\(_2\) 30.5, HfO\(_2\) - , MoO\(_3\) 6.4, B\(_2\)O\(_3\) 2.7, Mg 37.4 | 2060         | 8.3            | 35      |
| HMSB-1         | SiO\(_2\) 16.2, ZrO\(_2\) 23.0, HfO\(_2\) 29.9, MoO\(_3\) 5.5, B\(_2\)O\(_3\) 10.3, Mg 38.1 | 2119         | 9.3            | 31      |
| HMSB-2         | SiO\(_2\) 23.0, ZrO\(_2\) 23.0, HfO\(_2\) 30.5, MoO\(_3\) 6.4, B\(_2\)O\(_3\) 2.7, Mg 37.4 | 1750         | 8.4            | 34      |

Table 2 shows the calculated and experimentally determined phase compositions of the synthesized powders. One can see from table 2 that the main difference in the calculated and experimentally determined phase compositions of ZMSB-1 and ZMSB-2 powders is that ZrSi\(_2\) and ZrSi silicides are present instead of Zr\(_5\)Si\(_3\); ZrO\(_2\) oxide (~ 5%) is also present. The presence of the latter compound is attributed to heterogeneity of the initial mixtures, so its reduction during combustion is incomplete. The Zr\(_5\)Si\(_3\) compound is metastable and exists in a narrow temperature range. It decomposes at 1745°C via the eutectoid reaction [17]:

\[
\text{Zr}_5\text{Si}_3 \rightarrow \text{Zr}_3\text{Si}_2 + \text{Zr}_2\text{Si}
\]  

Therefore, the Zr\(_5\)Si\(_3\) phase can be present among the synthesis products only if they are rapidly cooled down or at a certain Zr : Si ratio (3:2; 5:3; 2:1) [18]; i.e., when the initial mixtures are enriched in zirconium. Since the Gibbs free energies of the reactions of formation of ZrSi and ZrSi\(_2\) at flame temperature are close (~133 and ~136 kJ, respectively), these reactions can be considered to be parallel. It is quite possible that the Zr : Si ratio also has an effect on presence of the ZrSi and ZrSi\(_2\)
phases in the powder. Hence, according to [18], ZrSi$_2$ is the main phase at a 1:2 Zr:Si ratio, while the contents of these two phases are equal at the 1:1 ratio. However, one needs to bear in mind that this study focuses on a multicomponent system, where Zr and Si are involved in formation of zirconium boride and molybdenum silicide. The fact that the initial oxides have different affinities for oxygen and, therefore, the rates of their reduction to pure components also differ, should also be taken into account. All these factors make it difficult to find the exact ratios between the components in the combustion wave and eventually the exact composition of the final products. For HMSB-1 and HMSB-2 powders, the calculated phase composition fully coincides with the experimentally determined one. ZrB$_2$/HfB$_2$, ZrSi$_2$/HfSi$_2$, ZrSi, and MoSi$_2$ are the main structural components of the synthesized powders; the ratio between these phases varies depending on contents of the initial components in the reaction mixtures.

### Table 2. Phase compositions of the SHS powders

| Composition no. | Calculated composition, wt.% | Experimental composition, wt.% |
|-----------------|-----------------------------|--------------------------------|
|                 | ZrB$_2$ | MoSi$_2$ | Zr$_2$Si$_3$ | ZrSi | Si | MgO | ZrB$_2$ | ZrSi$_2$ | ZrSi | MoSi$_2$ | Si | ZrO$_2$ |
| ZMSB-1          | 16    | 6      | 23     | -     | -  | 55  | 47  | 21   | 12  | 15     | -   | 5      |
| ZMSB-2          | 4     | 7      | -      | 39    | 7  | 43  | 10  | 37   | 32  | 16     | -   | 5      |
|                 | HfB$_2$ | MoSi$_2$ | HfSi$_2$ | Mg   | Si | MgO | HfB$_2$ | HfSi$_2$ | HfB | MoSi$_2$ | Si | -      |
| HMSB-1          | 14    | 4      | -      | 11    | 71 | 64  | -   | -    | 17  | 19     | -   | -      |
| HMSB-2          | 8     | 6      | 23     | 11    | 8  | 44  | 12  | 56   | 2   | 22     | 8   | -      |

One can infer from the results summarized in Table 3 that the powders have similar granulometric compositions. Whereas the maximum powder grain size before grinding was 33.7–78.2 µm and the average grain size was 10.3–15.0 µm, after grinding these values decreased to 23.3–34.1 and 6.1–8.1 µm, respectively.

### Table 3. The integral granulometric composition of the synthesized powders

| Composition no. | Grain size, µm |
|-----------------|----------------|
|                 | Before grinding | After grinding in a PCM |
|                 | $D_{10}$ | $D_{50}$ | $D_{90}$ | $D_{10}$ | $D_{50}$ | $D_{90}$ |
| ZMSB-1          | 3.0    | 11.3   | 58.3   | 14.7   | 0.9    | 5.6    | 34.1   | 8.0   |
| ZMSB-2          | 3.0    | 10.6   | 78.2   | 15.0   | 0.9    | 5.8    | 34.3   | 8.1   |
| HMSB-1          | 4.0    | 10.3   | 37.4   | 12.3   | 0.7    | 4.3    | 26.5   | 6.1   |
| HMSB-2          | 3.2    | 9.1    | 33.7   | 10.3   | 1.0    | 5.0    | 23.3   | 6.3   |

Figures 1a–1d show the typical microstructures and the granulometric distribution curves of the synthesized powders before and after grinding (for HMSB-1 powder as an example).

Prior to disintegration, the powders consisted of agglomerated particles > 25 µm in size that caused microstructural heterogeneity (Fig. 1a). The differential curves showed normal particle distribution with a single maximum (Fig. 1b). After grinding, the particle size decreased to 4–6 µm (Fig. 1c), which increased powder's homogeneity and shifted the maximum on the differential curve towards smaller particle sizes (Fig. 1d).

Table 4 summarizes the results of analyzing the phase composition of hot-pressed samples.

Identically to how it is in the synthesized powders (Table 2), the ZrB$_2$/HfB$_2$, ZrSi$_2$/HfSi$_2$ and MoSi$_2$ phases are the key components of the hot-pressed samples. The increased content of the ZrSi$_2$ phase in the hot-pressed ZMSB-1 and ZMSB-2 samples can be attributed to the fact that ZrSi becomes saturated with silicon during consolidation at a high temperature. Although the XRD data showed no unbound silicon within the structure of ZMSB-1 and ZMSB-2 powders, this element can exist in the amorphous state. The hot-pressed sample contained no HfB phase, which was present in the HMSB-2
powder. This phase is probably converted to HfB$_2$ during pressing as the content of HfB$_2$ in the consolidated sample increases. Zirconium silicate ZrSiO$_4$ in the ZMSB-1 powder can be formed via chemical interaction between zirconium oxide and silicon oxide. The latter compound can exist in the powder in an amorphous state due to its incomplete reduction during synthesis.

![Figure 1](image1)

**Figure 1.** The morphology and particle size of HMSB-1 powder (a, b) before and (c, d) after grinding.

| Composition no. | Phase content, wt.% |
|-----------------|---------------------|
|                 | ZrB$_2$ | ZrSi$_2$ | MoSi$_2$ | ZrO$_2$ | ZrSiO$_4$ |
| ZMSB-1          | 47      | 23       | 13       | 8       | 9         |
| ZMSB-2          | 18      | 61       | 16       | 5       | -         |
| ZMSB-1          | HfB$_2$ | HfSi$_2$ | MoSi$_2$ | HfB     | Si        |
| ZMSB-2          | 61      | -        | 23       | -       | 16        |
| HMSB-1          | 19      | 48       | 24       | -       | 9         |

**Table 4.** Phase composition of hot-pressed samples

Figure 2 shows the microstructures of the hot-pressed samples prepared from the synthesized powders.

The scanning electron microscopy (SEM) data are in good agreement with the findings obtained by XRD. The main structural components of the compacted samples are rectangular ZrB$_2$/HfB$_2$ grains with longitudinal size of 3–10 µm and ZrSi$_2$/HfSi$_2$ and MoSi$_2$ inclusions in the form of irregularly shaped coarse grains. The ZMSB-1 and ZMSB-2 samples also contain ZrO$_2$ and ZrSiO$_4$ oxides, which are indiscernible within the structure. In the ZMSB-2 sample, the dispersed MoSi$_2$ segregates are the inclusions located inside the ZrSi$_2$ phase, being typical of the eutectic.
After consolidation, the residual porosity of the samples is 1.1–7.4% and is dependent on the content of silicides in the synthesis products. The samples sintered from the powder with a higher content of silicides were characterized by lower porosity.

4. Conclusions
The heterophase $\text{ZrB}_2$–$\text{ZrSi}_2$–MoSi$_2$ and $\text{HfB}_2$–$\text{HfSi}_2$–MoSi$_2$ ceramics in the form of powders and materials consolidated to the residual porosity of 1.1–7.4% were produced by magnesiothermic synthesis followed by hot pressing. The ceramics have a composite structure with the average grain size of 6–8 µm. $\text{ZrB}_2$/$\text{HfB}_2$, $\text{ZrSi}_2$/$\text{HfSi}_2$, $\text{ZrSi}$ and MoSi$_2$, as well as a certain amount of the oxide phase, are the main phase components. The phase composition of the pressure-sintered dense samples almost coincides with that of the SHS powders. The ZMSB-1 and ZMSB-2 compositions are an exception: in these powders, the $\text{ZrSi}$ phase becomes saturated with silicon during hot pressing, eventually resulting in an increased content of the $\text{ZrSi}_2$ phase.

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References
[1] Silvestroni L, Failla S, Neshpor I and Grigoriev O 2018 J. Europ. Ceram. Soc. 38 2467–76
[2] Sonber J K, Murthy T S R C, Subramanian C, Kumar S, Fotedar R K and Suri A K 2011 Int. J. Refract. Met. Hard Mater. 29 21–30
[3] Levine S R, Opila E J, Halbig M C, Kiser J D, Singh M and Salem J A 2002 J. Europ. Ceram. Soc. 22 2757–67
[4] Fahrenholtz W G, Wuchina E J, Lee W E and Zhou Y 2014 *Ultra-high temperature ceramics: materials for extreme environment applications* ed (Wiley & Sons Inc.) p 441

[5] Pastor H 1997 *Metallic borides: preparation of solid bodies – sintering methods and properties of solid bodies* ed V I Matkovich (New York: Springer-Verlag) p 457–493

[6] Parthasarathy T A, Rapp R A, Opeka M M and Kerans R J 2008 *Mater. Sci. Forum* **595–598** 823–832

[7] Wang Z, Niu Y, Hu C, Li H, Zeng Y, Zheng X, Ren M and Sun J 2015 *Ceram. Int.* **41** 14868–75

[8] Silvestroni L, Meriggi G and Sciti D 2014 *Corros. Sci.* **83** 281–291

[9] Fei X, Niu Y, Ji H, Huang L and Zheng X 2010 *J. Therm. Spray Tech.* **19** 1074–80

[10] Potanin A Yu, Pogozhev Yu S, Levashov E A, Novikov AV, Shvindina N V and Sviridova T A 2017 *Ceram. Int.* **43** 10478–86

[11] Feng T, Li H-J, Shi X-H, Yang X, Li Y-X and Yao X-Y 2012 *Corros. Sci.* **60** 4–9

[12] Licheri R, Orrù R, Musa C and Cao G 2008 *Mater. Lett.* **62** 432–35

[13] Hu P, Gui K, Hong W and Zhang X 2017 *Mater. Lett.* **200** 14–17

[14] Rogachev A S and Mukasyan A S 2015 *Combustion for Materials Synthesis* (New York: Taylor and Francis) p 398

[15] Borovinskaya I P, Gromov A A, Levashov E A, Maksimov Y M, Mukasyan A S and Rogachev A S 2017 *Concise encyclopedia of self-propagating high-temperature synthesis. History, theory, technology, and products* Elsevier p 466

[16] Pogozhev Yu S, Iatsyuk I V, Potanin A Yu, Levashov E A, Novikov A V, Kochetov N A and Kovalev D Yu 2016 *Ceram. Int.* **42** 16758–65

[17] Lyakishev N P 2000 *State Diagrams of Binary Metal Systems* (Moscow: Mashinostroenie), p 448

[18] Bertolino N, Anselmi-Tamburini U, Maglia F, Spinolo G and Munir Z A 1999 *J. Alloys Comp.* **288** 238–248