



Article **Processing, Microstructure and Mechanical Properties of TiB₂-MoSi₂-C Ceramics**

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Abstract: Titanium boride (TiB₂) is a material classified as an ultra-high-temperature ceramic. The TiB₂ structure is dominated by covalent bonds, which gives the materials based on TiB₂ very good mechanical and thermal properties, making them difficult to sinter at the same time. Obtaining dense TiB₂ polycrystals requires a chemical or physical sintering activation. Carbon and molybdenum disilicide (MoSi₂) were chosen as sintering activation additives. Three series of samples were made, the first one with carbon additives: 0 to 4 wt.%; the second used 2.5, 5 and 10 wt.% MoSi₂; and the third with both additions of 2 wt.% carbon and 2.5, 5 and 10 wt.% MoSi2. On the basis of the dilatometric sintering analysis, all additives were found to have a favourable effect on the sinterability of TiB₂, and it was determined that sintering TiB₂ with the addition of carbon can be carried at 2100 $^{\circ}$ C and with MoSi₂ and both additives at 1800 °C. The polycrystals were sintered using the hot-pressing technique. On the basis of the studies conducted in this work, it was found that the addition of 1 wt.% of carbon allows single-phase TiB₂ polycrystals of high density (>90%) to be obtained. The minimum MoSi₂ addition, required to obtain dense sinters with a cermet-like microstructure, was 5 wt.%. High density was also achieved by the materials containing both additives. The samples with higher MoSi2 content, i.e., 5 and 10%, showed densities close to 100%. The mechanical properties, such as Young's modulus, hardness and fracture toughness (K_{Ic}), of the polycrystals and composites were similar for samples with densities exceeding 95%. The Vickers hardness was 23 to 27 GPa, fracture toughness (K_{IC}) was 4 to 6 MPa·m^{0.5} and the Young's modulus was 480 to 540 GPa. The resulting TiB₂-based materials showed potential in high-temperature applications.

Keywords: TiB₂; MoSi₂; carbon; UHTC; composites; mechanical properties

1. Introduction

Ceramic materials classified as ultra-high-temperature ceramics (UHTCs) are characterised by a high melting point, good mechanical properties at high temperature and high oxidation resistance. As they are increasingly used, more demands are put on them [1,2]. The group of materials classified as UHTCs includes metal borides in the fourth group of the periodic table of chemical elements, i.e., TiB₂, ZrB₂ and HfB₂. These borides have very high melting points (approx. 3000 °C), good thermal and electrical conductivity, high hardness, good mechanical properties and oxidation resistance. These valuable properties of AlB₂-type borides are the result of dominant covalent bonds present in their structure, which, on the other hand, has a negative effect on the sinterability of boride ceramics [1–4].



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Improved sinterability of boride ceramics is achieved by using sintering additives (sintering activators), such as nitrides TiN, AlN, Si₃N₄ or HfN [2,5–9]; carbides TaC, SiC, B₄C [2,10–15]; silicides MoSi₂, TiSi₂, TaSi₂ [4,16–23]; or oxides like ZrO₂ [24–28]. MoSi₂ and SiC are the most commonly used sintering activators for boride ceramics including TiB₂ [2,4,13,15–17,21]. The effect of silicide additives on the sinterability and properties of TiB₂ was, among others, studied by Raju, Murthy et al. [17,19]. Through the introduction of 2.5% MoSi₂ additive and the use of the hot-pressing technique, the authors of the discussed papers obtained dense composites at 1700 °C. According to the authors, MoSi₂ removes oxide impurities and then deforms the plasticity due to high temperature, filling the spaces between TiB₂ grains. In another paper, Murthy et al. [4] investigated the materials sintered by hot pressing with 0 to 25% MoSi₂ addition, leading to samples with density close to 98%, grain sizes of 2–5 μ m, high hardness of 25–27 GPa and fracture toughness of 5.1 MPa·m^{0.5}. The optimum amount of MoSi₂ was 10%, which resulted in a fine-grained microstructure of the sinters and hardness of 27 GPa.

Although carbon is a well-known additive that activates the sintering of covalent ceramics, it has been only marginally investigated for borides [29–31]. Also, the combination of carbon additives with other additives has been rarely studied [32–35]. Among others, Khoeini et al. [34] studied the effect of SiC and carbon on the sinterability of ZrB₂. The authors found that the addition of SiC effectively activates the sintering, but its simultaneous use with a small amount of carbon (1–2%) led to a lower addition of SiC and density close to 100%.

In the present study, it was decided to extend the state of knowledge on TiB₂ sintering. Investigations related to the influence of a combination of MoSi₂ and carbon additives on the sinterability of TiB₂ were carried out. The resulting high-density sinters were then tested with regard to their mechanical properties.

2. Materials and Experimental Procedure

The samples were prepared from commercial powders: TiB₂, ABCR Company, Germany (GRADE F, cat.no AB 134577); MoSi₂, Morton Thiokol, USA (99%, cat.no 48108). As a carbon precursor, phenol-formaldehyde resin of the NOVOLAK type (Chemical Plants Organika, Organika-Sarzyna, Poland) was used. During sintering, it undergoes pyrolysis, leaving 50 wt.% of amorphous carbon.

A reference sample of pure TiB_2 and three series of samples with various additive additions were made. The first series featured the addition of 1%, 2%, 3% and 4% wt. carbon; the second with the addition of 2.5%, 5% and 10% wt. $MoSi_2$; and the third one containing a constant amount of 2% wt. of carbon and 2.5%, 5% or 10% wt. of $MoSi_2$. The sample denominations used in this work are summarised in Table 1.

The Initial Composition	Name
TiB ₂	TB_0
TiB ₂ + 1% C	TB_1C
TiB ₂ + 2% C	TB_2C
TiB ₂ + 3% C	TB_3C
TiB ₂ + 4% C	TB_4C
$TiB_2 + 2.5\% MoSi_2$	TB_2.5MS
$TiB_2 + 5\% MoSi_2$	TB_5MS
$TiB_2 + 10\% MoSi_2$	TB_10MS
$TiB_2 + 2\% C + 2.5\% MoSi_2$	TB_2C_2.5MS
$TiB_2 + 2\% C + 5\% MoSi_2$	TB_2C_5MS
$TiB_2 + 2\% C + 10\% MoSi_2$	TB_2C_10MS

Table 1. Denomination of the samples.

The powder mixture components were weighed and then homogenised in ethanol in a ball mill for 12 h, using SiC spherical grinding media. Then, the alcohol was evaporated, and the powder mixtures were granulated by passing through a nylon 6 sieve. Cylindrical samples with a diameter of 12 mm and height 3–4 mm were formed through uniaxial double-ended pressing and then subjected to the dilatometric analysis.

The dilatometric sintering analysis was performed in a high-temperature graphite dilatometer of the authors' own construction. Sintering in the dilatometer was carried out in an argon flow with a heating rate 10 °C/min. The end of sintering happened when a characteristic *plateau* appeared on a linear dimensional change as a function of temperature. The dilatometric analysis enabled the final temperature of hot pressing to be determined.

The granulated powders were hot pressed using graphite dies under argon flow using Thermal Technology Inc. press model HP916-G-G. The reference sample and the samples with carbon addition were sintered at 25 MPa at 2100 °C, and the samples with MoSi₂ and MoSi₂ and carbon addition were sintered at 25 MPa at 1800 °C. All samples were kept at the final temperature for one hour. The heating rate in each case was 10 °C/min.

Apparent density of the sintered samples was measured using the Archimedes method. The relative density was calculated using 4.52 g/cm³ as the theoretical density of TiB₂. The surface of the samples was ground and polished using LaboPol (Struers, Champigny, France) polishing machine. Their microstructure was analysed using Scios2 DualBeam (ThermoFisher, Waltham, MA, USA) SEM microscope along with the EDS chemical analysis. The observations were made using the Circular Backscatter Electrons (CBS) detector.

In order to determine the phase composition, XRD analysis was performed with the X'Pert Pro apparatus (PANanlitycal, Malvern, UK). The quantitative phase composition of the sinters was determined using the Rietveld method. Hardness measurements were carried out by the Vickers method, using a FV-810 (Future-Tech, Tokyo, Japan) hardness tester. A standard load of 1 kg and an indenter pressing time of 10 s were used. Fracture toughness (K_{Ic}) was determined using the indentation method at 3 kg load. The Niihara formula (Equation (1)) was used to calculate the critical stress intensity factor (K_{Ic}).

$$K_{Ic} = 0.018 \cdot \frac{HV^{0.6} \cdot E^{0.4} \cdot 0.5d}{l^{0.5}}$$
(1)

where:

E—Young's modulus, MPa

HV—Vickers hardness, MPa

d-the indentation diagonal, m

l-mean radial cracks length, m

Young's modulus measurements were carried out using the ultrasonic method by measuring the velocity of transverse (C_T) and longitudinal (C_L) waves passing through the specimen with EPOCH 3 (Panametrics) ultrasonic defectoscope. The defectoscope, equipped with broadband ultrasonic transducers for longitudinal and transverse waves, was used to measure the transit times of the ultrasonic waves through the specimen. The transducers, characterised by short pulse durations, enable measurements on the specimens with small thicknesses to be carried out, eliminating overlapping of the successive pulses. Young's modulus was calculated from the velocities of ultrasonic wave propagation in the sample and density of the material (Equation (2)).

$$E = \rho \cdot C_{\rm T}^2 \frac{3C_{\rm L}^2 - 4C_{\rm T}^2}{C_{\rm L}^2 - C_{\rm T}^2}$$
(2)

where:

E—Young's modulus, GPa

C_L—velocity of the longitudinal ultrasonic wave, km/s

C_T—velocity of the transverse ultrasonic wave, km/s

 ρ —apparent density of the material, g/cm³

3. Results and Discussion

3.1. Dilatometric Analysis

Figure 1 shows the dilatometric sintering (sample shrinkage vs. temperature) curves, obtained for a series of samples with carbon addition and the reference sample. Sintering in the dilatometer was carried out up to 2150 °C, and despite such a high sintering temperature, sintering curves of the reference sample and the sample with 1 wt.% carbon addition do not show the *plateau* characteristic for the end of sintering.



Figure 1. Dilatometric sintering curves of the reference sample and samples with carbon addition.

Flattening of the sintering curve can be observed for the samples with a carbon addition higher than 1 wt.%. Sintering of the samples with carbon additions between 2 and 4 wt.% ends at ca. $2050 \,^{\circ}$ C.

Figure 2 presents the sintering curves of the samples with $MoSi_2$ and $MoSi_2$ and carbon addition.



Figure 2. Cont.



Figure 2. Dilatometric sintering curves of samples with (a) MoSi₂, (b) carbon and MoSi₂ additive.

The course of curves of the samples with MoSi₂ indicate that this addition effectively activates TiB₂ sintering (Figure 2a). When the MoSi₂ additive is 2.5 and 5 wt.%, the end of sintering occurs near 2100 °C, while a significant reduction in sintering temperature occurs when the additive is 10 wt.% because the temperature is close to 1950 °C. The best sintering results are given by the combination of carbon and MoSi₂ additives. For the samples containing 2 wt.% of carbon and 5 or 10 wt.% of MoSi₂, the characteristic *plateau*, indicating the end of sintering, occurs around 1700–1750 °C. The sample containing 2 wt.% carbon and 2.5 wt.% MoSi₂ addition shows the lowest linear shrinkage 8%, and its sintering ends near 1800 °C (Figure 2b). The beginning of sintering of the reference sample and the samples with carbon addition is in a range of 1300–1400 °C, while for the samples with MoSi₂ addition, it occurs in a temperature range of 1200–1350 °C. Based on the results of the dilatometric measurements, the temperature of hot pressing for the different samples was established.

3.2. Sintering of TiB₂ with Various Amounts of Carbon

The samples with carbon addition and the reference sample were sintered by hot pressing (HP) at 2100 °C. The relative density of the sinters is shown in Figure 3.

The reference sample shows the lowest relative density of 88%, and the introduction of 1 wt.% of carbon addition significantly increases the density (Figure 3). The highest density, around 98%, is achieved by the sinter with 2 wt.% carbon addition, while the density of the sinters with 3 and 4 wt.% carbon additions slightly decreases.

Figure 4 shows SEM microphotographs of the reference sample, the microstructure of which correlates with the measured density. The sample microstructure is inhomogeneous, and significant porosity is visible (black areas).

Figure 5 shows microstructures of the samples with carbon addition between 1% and 4%. The microstructures are homogeneous and characteristic for dense sinters. Black areas visible in the microstructure may be pores but also carbon or carbide inclusions, as confirmed by the EDS analysis (Figure 6).

In view of the XRD phase composition analysis, all the obtained polycrystals consist of 100% of TiB₂. Carbon and carbides may not be detected, as their amount in the composites may lay below the detection threshold of the XRD method.







Figure 4. SEM images of the reference TiB2 sample (TB_0) at low (a) and high (b) magnification.



Figure 5. SEM images of TiB₂ samples with carbon addition: (a) 1% C; (b) 2% C; (c) 3% C; (d) 4% C.



Figure 6. Chemical analysis of the black areas in the TiB₂ sample with 4 wt.% carbon addition.

3.3. Sintering of TiB₂ with Various Amounts of MoSi₂

TiB₂ samples with MoSi₂ additive were hot pressed at 25 MPa at 1800 °C. Figure 7 shows the dependence of relative density of the sinters on the amount of MoSi₂ additive. The lowest density, slightly lower than that of the reference sample, is shown by the composite with 2.5 wt.% MoSi₂ addition. A significant increase in density is observed for the samples with 5 and 10 wt.% addition of MoSi₂. Their relative density is 100%, which clearly indicates good sintering activation of TiB₂ by MoSi₂ (Figure 7).



Figure 7. Relative density of the sintered samples containing various amounts of MoSi₂.

Figure 8 shows SEM images of the TiB₂ composites containing MoSi₂. Their microstructures correlate well with the relative density. The highest porosity is found in the sample with the lowest amount, i.e., 2.5 wt.% of MoSi₂. The micrographs of the sample clearly show the presence of pores (the darkest areas) (Figure 8a). The number of black areas indicating the presence of pores in the samples with 5 and 10 wt.% MoSi₂ addition is relatively low (Figure 8b,c). It can be said that pores are absent in the sample with 5 wt.% MoSi₂ addition (Figure 8b).

Based on the XRD phase composition analysis (Table 2), it can be concluded that TiB_2 dominates in all samples. In the samples containing 2.5 wt.% and 5 wt.% $MoSi_2$, negligible amounts of MoC are also identified. In contrast, $MoSi_2$ and MoC can be identified in the sample containing 10 wt.% $MoSi_2$. The presence of molybdenum carbides is the result of a reaction between $MoSi_2$, oxide impurities and carbon from the graphite foil and the graphite die (HP).





Figure 8. SEM microphotographs of TiB_2 samples sintered with various amounts of $MoSi_2$ addition: 2.5 wt.% (a); 5.0 wt.% (b) and 10 wt.% (c).

Table 2. Quantitative phase composition of $TiB_2 + MoSi_2$ composites.

ICSInitial Phase Composition, wt.%	Phase Composition of the HP Sinters, wt. $\%$
97.5% TiB ₂ , 2.5% MoSi ₂	68.8% TiB ₂ 1, 29.7% TiB ₂ 2, 1.5% MoC
95% TiB ₂ , 5.0% MoSi ₂	69.8% TiB ₂ 1, 28.7% TiB ₂ 2, 1.5% MoC
90% TiB ₂ , 10% MoSi ₂	83.0% TiB ₂ 1, 9.4% TiB ₂ 2, 1.0% MoC, 6.6% MoSi ₂

Furthermore, in the light of the XRD analysis, titanium borides with the same structure but different lattice parameters are present in the composites (Table 3, TiB_2 1 and TiB_2 2).

Lattice	Theoretical Unit Cell	TiB ₂ + 2.5% MoSi ₂		TiB ₂ + 5.0% MoSi ₂		TiB ₂ + 10% MoSi ₂	
Parameter, Å	Parameters of TiB ₂ , [36]	TiB ₂ 1	TiB ₂ 2	TiB ₂ 1	TiB ₂ 2	TiB ₂ 1	TiB ₂ 2
а	3.028	3.030	3.028	3.030	3.030	3.029	3.029
b	3.028	3.030	3.028	3.030	3.030	3.029	3.029
с	3.228	3.230	3.230	3.230	3.231	3.231	3.230

TiB₂ 1 and TiB₂ 2—TiB₂ with the same structure but different lattice parameters.

The differences in hues of grey visible in the SEM images indicate differences in the chemical composition of individual areas of the samples. Figure 9 shows the result of a local chemical composition analysis of the TiB_2 composite containing 10 wt.% MoSi₂, and the results of the chemical composition analysis are consistent with the results of the phase composition analyses of the sample (Table 2).



Quantitative analysis, % at.



Quantitative analysis, % at.



Quantitative analysis, % at. % B – 34.1



Quantitative analysis, % at. % O – 74.6



Figure 9. Results of the point chemical analysis EDS of TiB₂ samples with 10 wt.% MoSi₂ addition (**a–d**) (chemical analysis was carried out at the points marked by red arrows on the SEM images).

In the sinters, grains cores rich in titanium and boron can be identified, which are most likely titanium diboride (Figure 9a). There are also areas in which, in addition to titanium, molybdenum and carbon (Figure 9b) as well as molybdenum and silicon (Figure 9c) can be found. An increased amount of molybdenum is identified in light-grey areas around TiB₂ grains (Figure 9c). There are also the darkest areas, which, in many cases, are pores but not always, as Figure 9d shows. In many such areas, significant amounts of oxygen and silicon can be identified. The reaction between MoSi₂ and the oxides which passivate the boride grains can result in the formation of an amorphous phase from the Si-O-B system [37–39].

3.4. Sintering of TiB₂ with 2 wt.% Carbon Addition and Various Amounts of MoSi₂

 TiB_2 samples, containing 2 wt.% carbon and different $MoSi_2$ additions, were hot pressed at 1800 °C. The relative densities of the resulting polycrystals are shown in Figure 10.





The lowest density ca. 90% was exhibited by the sample with the lowest $MoSi_2$ content. An increase in $MoSi_2$ addition to 5 wt.% led to composites with densities higher than 98%. The relative density of 100% was achieved by the composite with the highest $MoSi_2$ addition, i.e., 10 wt.% (Figure 10).

The combination of carbon and MoSi₂ additions results in significantly increased density of the composite with 2.5 wt.% MoSi₂ addition, as compared to the analogous composite without carbon addition (Figure 7).

Figure 11 shows SEM microstructures of the TiB₂ samples with a simultaneous addition of carbon and MoSi₂. In the sample with 2.5 wt.% MoSi₂ addition, significant porosity is visible (darkest areas). A homogeneous, dense microstructure is presented by the samples with 5 and 10 wt.% MoSi₂ additions (Figure 11b,c). Again, the microstructure of TiB₂ composites with carbon and different amounts of MoSi₂ addition is similar to the one typical for cermets [40], i.e., grains consisting of cores and characteristic shells (Figure 11).

According to the results of XRD phase composition analysis, the composites after sintering are dominated by titanium boride with different elemental cell sizes (Tables 4 and 5). The presence of two hexagonal TiB₂ phases (here named TiB₂ 1 and TiB₂ 2) with different lattice parameters may indicate substitutions within the boride cell by the additive-derived elements, i.e., Mo, Si and C. Furthermore, MoSi₂ is not present after sintering. It is likely that during sintering, chemical reactions occur between TiB₂, the oxide impurities,



i.e., TiO_2 and B_2O_{3} , and the additives, i.e., $MoSi_2$ and carbon. These reactions resulted in the formation of silicon carbide and complex carbide (Ti, Mo)C₂ (Table 4).

Figure 11. SEM images of TiB_2 samples with 2% carbon and different amounts of $MoSi_2$ addition: 2.5% (**a**), 5.0% (**b**) and 10% (**c**).

Table 4. Quantitative phase composition of $TiB_2 + 2\%C + x\%MoSi_2$ composites.

Initial Phase Composition, wt.%	Phase Composition of the HP Sinters, wt.%
95.5% TiB ₂ , 2.0% C, 2.5% MoSi ₂	96.8% TiB ₂ 1, 0.1% TiB ₂ 2, 1.7% TiC, 1.4% SiC
93% TiB ₂ , 2.0% C, 5.0% MoSi ₂	66.3% TiB ₂ 1, 28.9% TiB ₂ 2, 1.8% SiC, 3.0% (Ti,Mo)C ₂
88% TiB ₂ , 2.0% C, 10% MoSi ₂	76.1% TiB ₂ 1, 18.6% TiB ₂ 2, 3.1% SiC, 2.2% (Ti,Mo)C ₂

Table 5. Lattice parameters of titanium boride phases identified in $TiB_2 + 2\% C + x\% MoSi_2$ composites.

Lattice Parameter,	Theoretical Unit Cell	TiB ₂ + 2%C +2.5% MoSi ₂		TiB ₂ + 2%C +5.0% MoSi ₂		TiB ₂ + 2%C +10% MoSi ₂	
Å	Parameters of $I1B_2$, $[36]$	TiB ₂ 1	TiB ₂ 2	TiB ₂ 1	TiB ₂ 2	TiB ₂ 1	TiB ₂ 2
а	3.028	3.027	3.034	3.029	3.027	3.029	3.027
b	3.028	3.027	3.034	3.029	3.027	3.029	3.027
с	3.228	3.233	3.220	3.230	3.231	3.230	3.232

 TiB_2 1 and TiB_2 2— TiB_2 with the same structure but different lattice parameters.

The EDS chemical analysis of the selected sample (TB_2C_10MS) is shown in Figure 12. The darkest areas could be pores but also oxide or carbide grains since the areas are rich in oxygen, carbon, silicon and titanium as well as molybdenum. The dark-grey areas (cores) are most likely TiB₂ grains, while the light-coloured grain shells and grain boundary areas are rich in molybdenum, titanium, boron and, in some places, also carbon.



Figure 12. EDS element distribution maps of the TB_2C_10MS composite.

3.5. Mechanical Properties of the TiB₂-MoSi₂-C Ceramics

The composites were tested for Vickers hardness, critical stress intensity factor (K_{Ic}), which is a measure of fracture toughness, and Young's modulus. Due to the highly subjective measurement of the critical stress intensity factor using the indentation method, this was carried out on the composites with a relative density higher than 95%. The obtained results are summarised in Table 6.

Sample	Sintering Temperature (HP), °C	Relative Density, % (*)	Vickers Hardness, GPa	Fracture Toughness, MPa∙m ^{0.5}	Young's Modulus, GPa
TB_0	2150	88.2 ± 0.3	19.09 ± 6.30	-	-
TB_1C	2150	94.3 ± 0.1	26.31 ± 5.86	-	526 ± 12
TB_2C	2150	97.8 ± 0.1	25.31 ± 0.77	5.16 ± 0.28	536 ± 9
TB_3C	2150	96.9 ± 0.4	23.34 ± 2.17	5.26 ± 0.47	496 ± 16
TB_4C	2150	95.9 ± 0.3	25.68 ± 5.29	5.52 ± 0.20	542 ± 10
TB_2.5MS	1800	84.3 ± 0.6	16.97 ± 2.86	-	-
TB_5MS	1800	98.5 ± 0.2	26.21 ± 2.25	6.25 ± 0.51	536 ± 11
TB_10MS	1800	100.0 ± 0.4	26.78 ± 3.37	4.86 ± 0.19	504 ± 24
TB_2C_2.5MS	1800	89.1 ± 0.8	17.19 ± 1.87	-	440 ± 14
TB_2C_5MS	1800	98.8 ± 0.4	24.88 ± 2.03	4.79 ± 0.52	543 ± 6
TB_2C_10MS	1800	100.0 ± 0.2	24.41 ± 1.90	4.17 ± 0.31	533 ± 12

Table 6. Relative density and selected mechanical properties of the materials.

(*) the theoretical density of TiB2 was 4.52 g/cm^3 .

The hardness of the samples with the lowest densities, i.e., the reference sample (TB_0), with 2.5% MoSi₂ addition (TB_2.5MS) and with 2% carbon and 2.5% MoSi₂ addition, is not higher than 20 GPa (Table 6). The introduction of 1% carbon results in a noticeable increase in hardness to 26 GPa. The hardness of composites with 1 to 4% carbon addition is similar and ranges from 23 to 26 GPa. For the composites with MoSi₂ addition, the lowest hardness is shown by TB_2.5MS and TB_2C_2.5MS samples. For other composites with MoSi₂ addition, the hardness ranges from 24 to 26 GPa.

Based on the measured values of the critical stress intensity factor (Table 6), it can be concluded that the composites exhibit high fracture toughness. The lowest K_{Ic} values, larger than 4 MPa·m^{0.5}, are shown by the composites with both additives, i.e., carbon and MoSi₂ additives. The K_{Ic} values, close to 5 MPa·m^{0.5}, are exhibited by the composites with carbon additions of 2 to 4%. In contrast, K_{Ic} values between 4.86 and 6.25 MPa·m^{0.5} are shown by the composites with the MoSi₂ additive.

The Young's modulus values of all composites are high, ranging from 496 GPa for the TB_3C composite to 543 GPa for the TB_2C_5MS composite.

4. Results and Discussion

On the basis of the results of these investigations, a favourable effect of all used additives, i.e., carbon, MoSi₂ and MoSi₂+C, on the sinterability of TiB₂ titanium diboride was found. Firstly, a dilatometric sintering analysis was carried out, which showed the validity of the abovementioned sintering activators (Figures 1 and 2). Furthermore, it is clear from the dilatometric measurements that the use of 10% MoSi₂ addition and the combination of both additives significantly reduces the sintering temperature of TiB₂ (Figure 2). The sintering temperature of polycrystals with carbon and MoSi₂ additives does not exceed 1800 °C. For the polycrystals with MoSi₂, only a 10% addition of MoSi₂ reduces the sintering temperature to 1900 °C (Figure 2).

According to the dilatometric sintering analysis, the hot-pressing temperatures of all composites were determined. The composites with carbon as well as the reference sample were hot pressed at 2100 °C, while the composites with MoSi₂ and the composites with carbon and MoSi₂ were hot pressed at 1800 °C. In many cases, polycrystals with a relative density of 100% were obtained. In the case of carbon addition, the highest densities were obtained when the carbon addition was between 2 and 4 wt.%. Dense polycrystals were produced by adding 5 or 10 wt.% MoSi₂ as well as 2 wt.% carbon together with 5 or 10 wt.% MoSi₂ (Figures 3, 7 and 10).

Most of the obtained polycrystals (sinters) were non-porous, as can be seen from the microstructure analysis (Figures 5, 8 and 11), while it cannot be deduced from the apparent density measurements and relative density calculations (Table 6). One of the main reasons for the precise calculation of the theoretical density is the numerous reactions that take place during sintering between TiB₂, MoSi₂, carbon and oxide impurities, resulting in the formation of new phases, as confirmed by the results of the phase composition analysis (Tables 2 and 4). Therefore, taking the density calculated from the initial compositions as the theoretical density from the phase composition analysis, due to the presence of solid solutions and amorphous phases, is also erroneous. For the sake of comparison, a single value of the theoretical density was used, and the theoretical density of TiB₂, i.e., 4.52 g/cm³, was taken as the theoretical density. High density of the sinters was indirectly evidenced by water absorption measurements (Table 7). Water absorption of many polycrystals reaches only a few hundredths of one percent and is indicative of the lack of open porosity in these materials.

Sample	Water Asorbability, %
TB_0	0.03 ± 0.01
TB_1C	0.03 ± 0.01
TB_2C	0.01 ± 0.02
TB_3C	0.15 ± 0.04
TB_4C	0.08 ± 0.03
TB_2.5MS	3.69 ± 0.50
TB_5MS	0.05 ± 0.02
TB_10MS	0.04 ± 0.01
TB_2C_2.5MS	1.29 ± 0.20
TB_2C_5MS	0.08 ± 0.02
TB_2C_10MS	0.06 ± 0.01

Table 7. Water absorbability of the materials.

The addition of carbon enables single-phase polycrystals to be obtained, as evidenced by the phase composition analysis, according to which only TiB₂ is present in such sinters. Also, the microstructures shown in Figure 5 are characteristic of single-phase and dense sinters when carbon addition is in a range of 2 to 4 wt.%. Phase composition analyses demonstrate the effectiveness of using carbon as an oxide impurity reducer. According to the literature [41], carbon can react both with B₂O₃ and SiO₂ at the temperatures close to 1000 °C in low vacuum (20 Pa). The local EDS analysis of the chemical composition, carried out during SEM observations, showed the trace presence of fine particles, whose chemical composition suggests that they may be the particles of carbon or boron and titanium carbides (Figure 6).

Carbon in the sintering of covalent ceramics acts as a reducer of oxide impurities [29–35]. When it was intentionally added, the reaction between oxide impurities, i.e., SiO_2 or TiO_2 , resulted in the formation of SiC and TiC and complex titanium-molybdenum carbide,

respectively (Table 4). When carbon addition was not intentionally added, the favoured reaction was the formation of MoC. In this case, carbon can be regarded as an impurity from the system with which sintering was carried out, i.e., from the heating element, matrix or graphite film. In addition, in composites with only MoSi₂, oxide impurities are present in the form of an amorphous Si-O-B-Ti-Mo phase, which is not identified by XRD analysis but visible in SEM images (Figures 9d and 12).

The phase composition of the polycrystals sintered with MoSi₂ (Table 2) and with carbon and MoSi₂ additives shows that such composites (Table 4) were obtained, in which two TiB₂ phases with different lattice parameters dominated (Tables 3 and 5). In addition, molybdenum carbide was identified in all composites sintered with MoSi₂ only, and only the sample with the highest $MoSi_2$ addition showed the presence of this additive. In contrast, for the composites with both additives, the two titanium boride phases with different lattice parameters were dominant (Table 5, Supplementary Materials). Silicon and titanium carbides were also identified in these composites, and a complex carbide with the formula (Mo,Ti)C₂ was found in the samples with 5 and 10% wt. MoSi₂ additions. Substitutions of titanium ($a_r = 140 \text{ pm}$) by Mo ($a_r = 145 \text{ pm}$), Si ($a_r = 145 \text{ pm}$) cations as well as boron ($a_r = 75 \text{ pm}$) by carbon ($a_r = 70 \text{ pm}$) can led to the presence of hexagonal titanium boride phases with different lattice parameters or, in other words, to the presence of solid solutions [42]. The presence of $(Mo,Ti,Si)B_2$ solid solutions can be evidenced by a microstructure similar to that of *core-shell* cermets [40]. This type of microstructure is often found in composites based on metal borides in the fourth group of the periodic table of chemical elements [21-23,43-46]. SEM photographs of TB_MS and TB_C_MS composites (Figures 8 and 11) show microstructures similar to those typical for cermets. The microstructure of cermets typically consists of particles with "hard cores" and solid solution layers on their surface ("shells"). In typical cermets, such *core-shell* particles are joined together by bonding metals, e.g., cobalt [22,23,44,46]. With regard to the TiB₂-MoSi₂-C composites studied, it can be assumed that the cores are formed by one of the titanium boride phases with the shell by the titanium boride solid solution with substitutions (Figure 13).



Figure 13. SEM microstructure of the composite with 10 wt.% MoSi₂ addition characteristics of cermets.

The EDS chemical element distribution maps, made during the SEM observations, showed further that, in both groups of composites with the $MoSi_2$ additive, there are areas enriched in oxygen and silicon (Figures 9 and 12). During sintering, a variety of reactions can occur in all composites, including the carbothermal reduction of oxides, passivating boride particles (Equations (3) and (4)), and the reactions between $MoSi_2$ and

$$TiO_2 + 3C \rightarrow TiC + 2CO \uparrow$$
 (3)

$$2B_2O_3 + 7C \to B_4C + 6CO \uparrow \tag{4}$$

$$2MoSi_2 + 2B_2O_3 + TiO_2 \rightarrow TiB_2 + 4SiO_2 + 2MoB \tag{5}$$

$$2MoSi_2 + 2B_2O_3 + 2.5C \to 2.5SiC + 1.5SiO_2 + 2MoB \tag{6}$$

$$5MoSi_2 + 7O_2 \rightarrow Mo_5Si_3 + 7SiO_2 \tag{7}$$

As shown by the composite microstructures in Figures 8 and 11, solid solutions can be formed at grain boundaries or, more commonly, at the surface of the boride grains. The literature reports that the formation of the solid solutions in question can be related to the presence of liquid phases with the compositions resulting from the initial chemical composition of the composites [1,17,21,44,47,49–51]. The most likely formation of liquid phases is from the Si–B–O system, in which the elements (Ti, Mo), forming the components of the composite, can dissolve. It should be added that in the case of the MoSi₂ additive alone, the passivating oxides do not reduce as readily as under the influence of carbon. During cooling, the epitaxial precipitation from the liquid phase and the formation of solid solutions can occur [4,17,21,44,51]. The occurrence of the solid solutions discussed, as well as silicide, carbide and SiO₂ phases, may be indirect evidence of the presence of liquid phases during the sintering of composites with MoSi₂ addition. Furthermore, oxygen-rich and silicon-rich particles were identified during the chemical composition analysis, even when MoSi₂ and carbon were used as additives (Figure 12).

According to the literature [37–39], the occurrence of liquid phases from the Si–B– O system is mainly possible in boride composites with silicide additives. These phases can effectively support sintering under pressure by facilitating, among other things, the movement of grains relative to each other [52]. In this case, if the oxides are not fully reduced, even when a small addition of carbon is introduced, it is possible for a reaction between SiO₂ and B_2O_3 to take place, resulting in the formation of a liquid phase from the Si–B–O system, in which elements present in the initial compounds forming the composites can dissolve.

Furthermore, the sintering temperature of composites with $MoSi_2$ is $1800 \degree C$ and does not exceed the melting point of the silicide ($T_m = 2050 \degree C$) [50,53] but, as reported in the literature [52–55], at a temperature higher than 800 °C, silicides, including $MoSi_2$, deform plastically and can fill pores during sintering.

The relationship between the density of the composites and the values of the tested mechanical properties is observed. The composites with the highest density, regardless of the additive used, show high Vickers hardness of 23 to 26 Gpa. Also, in terms of fracture toughness, all the composites tested show a high value of the critical stress intensity factor K_{Ic} (Table 6). The lowest values of K_{Ic} from 4.18 to 4.79 Mpa·m^{0.5} are exhibited by the composites with two additives, fracture toughness of composites with 2 to 4 wt.% carbon addition oscillates around 5 Mpa·m^{0.5}, while in the composites with MoSi₂, it ranges from 6.25 to 4.86 Mpa·m^{0.5} for 5 wt.% MoSi₂ and 10 wt.% MoSi₂ addition, respectively. The typical phenomena leading to the increase in effective fracture energy are observed in composites, such as intergranular cracking (Figure 14a,c), crack deflection as well as crack defragmentation (Figure 14e,f). It is noteworthy that the grain boundaries (bonding phase) in the composites with 5 wt.% MoSi₂ addition are weaker than those in the composites with 10 wt.% MoSi₂ addition (compare Figure 14a with Figures 14b and 14c with Figure 14d). This results in a lower value of the critical stress intensity factor in the composites with 10 wt.% MoSi₂ addition (Table 6). The fracture then runs predominantly through the grains as well as along the TiB_2 grain boundaries (Figure 14b,d).



Figure 14. Course of cracks in composites: (a) TB2_5MS; (b) TB2_10MS; (c) TB_2C_5MS; (d) TB_2C_10MS; (e) TB_3C; and (f) TB_4C.

All high-density composites can be classified as low-deformability materials, as evidenced by the high values of their Young's modulus (Table 6).

The values of hardness, fracture toughness and Young's modulus shown for the investigated composites are similar to and often better than those reported in the literature [4,16,47,56].

5. Conclusions

- 1. The hot pressing of TiB₂ with MoSi₂ or carbon and MoSi₂ with carbon resulted in single-phase polycrystals and composites with density higher than 95%. Both additives used can be considered as TiB₂ sintering activators.
- 2. It is noteworthy that the use of MoSi₂ as a sintering activating additive significantly reduces the sintering temperature of titanium boride down to 1800 °C.
- 3. With the addition of carbon, it is possible to obtain single-phase polycrystals, in which only the TiB₂ phase is present. On the other hand, with the addition of MoSi₂ as well

as the combined addition of MoSi₂ and carbon, it is possible to obtain solid composites with a *core–shell* microstructure, characteristic for cermets.

- 4. Carbon is an effective reducer of oxide impurities during TiB₂ sintering.
- 5. Due to the presence of liquid phases from the Si–B–O–Mo system and plastic deformation of MoSi₂, it becomes possible to obtain dense composites based on TiB₂.
- 6. The produced materials have potential in high-temperature applications due to the high melting point of TiB₂ and very good properties, such as high hardness, high fracture toughness and low deformability. Nevertheless, further testing of their thermal and chemical properties is required.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/cryst14030212/s1, Figure S1: An example of a reflection indicating the presence of two titanium borides with different lattice parameters, Figure S2: Differences between the actual (red curve) and theoretical (blue curve) curves, indicating a significant error on the XRD analysis, Figure S3: High theoretical and real curve fit in XRD analysis, Figure S4. XRD pattern of TB_0 sample, Figure S5. XRD pattern of TB_4C sample, Figure S6. XRD pattern of TB_10MS composite and Figure S4. Figure S7, XRD pattern of TB_2C_10MS composite.

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References

- Basu, B.; Raju, G.B.; Suri, A.K. Processing and Properties of Monolithic TiB₂ Based Materials. *Int. Mater. Rev.* 2006, *51*, 352–374. [CrossRef]
- Golla, B.R.; Mukhopadhyay, A.; Basu, B.; Thimmappa, S.K. Review on Ultra-High Temperature Boride Ceramics. *Prog. Mater. Sci.* 2020, 111, 100651. [CrossRef]
- Fahrenholtz, W.G.; Hilmas, G.E. Ultra-High Temperature Ceramics: Materials for Extreme Environments. Scr. Mater. 2017, 129, 94–99. [CrossRef]
- Murthy, T.S.R.C.; Basu, B.; Balasubramaniam, R.; Suri, A.K.; Subramanian, C.; Fotedar, R.K. Processing and Properties of TiB₂ with MoSi₂ Sinter-Additive: A First Report. J. Am. Ceram. Soc. 2006, 89, 131–138. [CrossRef]
- Monteverde, F.; Bellosi, A. Efficacy of HfN as Sintering Aid in the Manufacture of Ultrahigh-Temperature Metal Diborides-Matrix Ceramics. J. Mater. Res. 2004, 19, 3576–3585. [CrossRef]
- Monteverde, F.; Bellosi, A. Effect of the Addition of Silicon Nitride on Sintering Behaviour and Microstructure of Zirconium Diboride. Scr. Mater. 2002, 46, 223–228. [CrossRef]
- Monteverde, F.; Bellosi, A. Beneficial Effects of AlN as Sintering Aid on Microstructure and Mechanical Properties of Hot-pressed ZrB₂. Adv. Eng. Mater. 2003, 5, 508–512. [CrossRef]
- Li, L.-H.; Kim, H.-E.; Son Kang, E. Sintering and Mechanical Properties of Titanium Diboride with Aluminum Nitride as a Sintering Aid. J. Eur. Ceram. Soc. 2002, 22, 973–977. [CrossRef]
- 9. Park, J.; Koh, Y.; Kim, H.; Hwang, C.S.; Kang, E.S. Densification and Mechanical Properties of Titanium Diboride with Silicon Nitride as a Sintering Aid. *J. Am. Ceram. Soc.* **1999**, *82*, 3037–3042. [CrossRef]

- 10. Bhaumik, S.K.; Divakar, C.; Singh, A.K.; Upadhyaya, G.S. Synthesis and Sintering of TiB₂ and TiB₂–TiC Composite under High Pressure. *Mater. Sci. Eng. A* 2000, 279, 275–281. [CrossRef]
- 11. Kang, E.S.; Kim, C.H. Improvements in Mechanical Properties of TiB₂ by the Dispersion of B₄C Particles. *J. Mater. Sci.* **1990**, *25*, 580–584. [CrossRef]
- 12. Kang, E.S.; Jang, C.W.; Lee, C.H.; Kim, C.H.; Kim, D.K. Effect of Iron and Boron Carbide on the Densification and Mechanical Properties of Titanium Diboride Ceramics. *J. Am. Ceram. Soc.* **1989**, 72, 1868–1872. [CrossRef]
- Rodríguez-Rojas, F.; Zamora, V.; Guiberteau, F.; Ortiz, A.L. Solid-State Spark Plasma Sintering of Super Wear Resistant B₄C–SiC– TiB₂ Triplex-Particulate Composites. *Ceram. Int.* 2023, 49, 5532–5537. [CrossRef]
- 14. Torizuka, S.; Sato, K.; Harada, J.; Yamamoto, H.; Nishio, H. Microstructure and Sintering Mechanism of TiB₂-ZrO₂-SiC Composite. *J. Ceram. Soc. Jpn.* **1992**, *100*, 392–397. [CrossRef]
- Torizuka, S.; Sato, K.; Nishio, H.; Kishi, T. Effect of SiC on Interfacial Reaction and Sintering Mechanism of TiB₂. J. Am. Ceram. Soc. 1995, 78, 1606–1610. [CrossRef]
- Mukhopadhyay, A.; Raju, G.B.; Basu, B. Understanding Influence of MoSi₂ Addition (5 Weight Percent) on Tribological Properties of TiB₂. *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 2008, 39, 2998–3013. [CrossRef]
- 17. Murthy, T.S.R.C.; Balasubramaniam, R.; Basu, B.; Suri, A.K.; Mungole, M.N. Oxidation of Monolithic TiB₂ and TiB₂–20wt.% MoSi₂ Composite at 850 °C. *J. Eur. Ceram. Soc.* **2006**, *26*, 187–192. [CrossRef]
- 18. Murthy, T.S.R.C.; Sonber, J.K.; Subramanian, C.; Fotedar, R.K.; Kumar, S.; Gonal, M.R.; Suri, A.K. A New TiB₂+CrSi₂ Composite— Densification, Characterization and Oxidation Studies. *Int. J. Refract. Met. Hard. Mater.* **2010**, *28*, 529–540. [CrossRef]
- 19. Raju, G.B.; Basu, B. Densification, Sintering Reactions, and Properties of Titanium Diboride With Titanium Disilicide as a Sintering Aid. *J. Am. Ceram. Soc.* 2007, *90*, 3415–3423. [CrossRef]
- 20. Raju, G.B.; Mukhopadhyay, A.; Biswas, K.; Basu, B. Densification and High-Temperature Mechanical Properties of Hot Pressed TiB₂-(0-10 Wt.%) MoSi₂ Composites. *Scr. Mater.* **2009**, *61*, 674–677. [CrossRef]
- 21. Silvestroni, L.; Kleebe, H.-J.; Lauterbach, S.; Müller, M.; Sciti, D. Transmission Electron Microscopy on Zr- and Hf-Borides with MoSi₂ Addition: Densification Mechanisms. *J. Mater. Res.* **2010**, *25*, 828–834. [CrossRef]
- Sciti, D.; Silvestroni, L.; Celotti, G.; Melandri, C.; Guicciardi, S. Sintering and Mechanical Properties of ZrB₂–TaSi₂ and HfB₂–TaSi₂ Ceramic Composites. J. Am. Ceram. Soc. 2008, 91, 3285–3291. [CrossRef]
- Silvestroni, L.; Sciti, D. Densification of ZrB₂-TaSi₂ and HfB₂-TaSi₂ Ultra-High-Temperature Ceramic Composites. J. Am. Ceram. Soc. 2011, 94, 1920–1930. [CrossRef]
- 24. Watanahe, T.; Shoubu, K. Mechanical Properties of Hot-Pressed TiB₂-ZrO₂ Composites. J. Am. Ceram. Soc. **1985**, 68, C-34. [CrossRef]
- Telle, R.; Meyer, S.; Petzow, G.; Franz, E.D. Sintering Behaviour and Phase Reactions of TiB₂ with ZrO₂ Additives. *Mater. Sci. Eng.* A 1988, 105–106, 125–129. [CrossRef]
- Schneider, J.; Zum Gahr, K.-H.; Müller, R.; Franz, E.-D. Einfluß Des ZrO2₂ -Zusatzes Auf Mechanische Eigenschaften Und Den Ungeschmierten Gleitverschleiß von TiB₂-ZrO₂-Mischkeramiken. *Materwiss Werksttech* 1996, 27, 359–366. [CrossRef]
- Muraoka, Y.; Yoshinaka, M.; Hirota, K.; Yamaguchi, O. Hot Isostatic Pressing of TiB₂-ZrO₂(2 Mol% Y2O3) Composite Powders. *Mater. Res. Bull.* 1996, 31, 787–792. [CrossRef]
- Graziani, T.; Bellosi, A. Sintering and Characterization of TiB₂-B₄C-Zr0₂ Composites. *Mater. Manuf. Process.* 1994, *9*, 767–780. [CrossRef]
- 29. Stobierski, L.; Gubernat, A. Sintering of Silicon CarbideI. Effect of Carbon. Ceram. Int. 2003, 29, 287–292. [CrossRef]
- 30. Gubernat, A. Pressureless Sintering of Single-Phase Tantalum Carbide and Niobium Carbide. *J. Eur. Ceram. Soc.* **2013**, *33*, 2391–2398. [CrossRef]
- Kornaus, K.; Rączka, M.; Gubernat, A.; Zientara, D. Pressureless Sintering of Binderless Tungsten Carbide. J. Eur. Ceram. Soc. 2017, 37, 4567–4576. [CrossRef]
- Zhang, S.C.; Hilmas, G.E.; Fahrenholtz, W.G. Pressureless Sintering of ZrB₂–SiC Ceramics. J. Am. Ceram. Soc. 2008, 91, 26–32.
 [CrossRef]
- 33. Zhu, S.; Fahrenholtz, W.G.; Hilmas, G.E.; Zhang, S.C. Pressureless Sintering of Zirconium Diboride Using Boron Carbide and Carbon Additions. *J. Am. Ceram. Soc.* 2007, *90*, 3660–3663. [CrossRef]
- Khoeini, M.; Nemati, A.; Zakeri, M.; Tamizifar, M.; Samadi, H. Comprehensive Study on the Effect of SiC and Carbon Additives on the Pressureless Sintering and Microstructural and Mechanical Characteristics of New Ultra-High Temperature ZrB₂ Ceramics. *Ceram. Int.* 2015, 41, 11456–11463. [CrossRef]
- 35. Brown-Shaklee, H.J.; Fahrenholtz, W.G.; Hilmas, G.E. Densification Behavior and Microstructure Evolution of Hot-Pressed HfB₂. *J. Am. Ceram. Soc.* **2011**, *94*, 49–58. [CrossRef]
- ICSD (Inorganic Crystal Structure Database) Card 98-003-0330 of Titanium Boride, (n.d.). Available online: https://icsd.products. fiz-karlsruhe.de/ (accessed on 1 February 2024).
- 37. Singh, M.; Wiedemeier, H. Chemical Interactions in Diboride-Reinforced Oxide-Matrix Composites. J. Am. Ceram. Soc. 1991, 74, 724–727. [CrossRef]
- Harrington, G.J.K.; Hilmas, G.E.; Fahrenholtz, W.G. Effect of Carbon and Oxygen on the Densification and Microstructure of Hot Pressed Zirconium Diboride. J. Am. Ceram. Soc. 2013, 96, 3622–3630. [CrossRef]
- 39. BAIK, S.; BECHER, P.F. Effect of Oxygen Contamination on Densification of TiB₂. J. Am. Ceram. Soc. 1987, 70, 527–530. [CrossRef]

- 40. García, J.; Collado Ciprés, V.; Blomqvist, A.; Kaplan, B. Cemented Carbide Microstructures: A Review. *Int. J. Refract. Met. Hard. Mater.* **2019**, *80*, 40–68. [CrossRef]
- 41. Yan, Y.; Huang, Z.; Dong, S.; Jiang, D. Pressureless Sintering of High-Density ZrB₂ –SiC Ceramic Composites. *J. Am. Ceram. Soc.* **2006**, *89*, 3589–3592. [CrossRef]
- 42. 8.2: Atomic and Ionic Radius, (n.d.). Available online: https://Chem.Libretexts.Org/@go/Page/98634?Pdf (accessed on 14 October 2023).
- Paul, T.R.; Mondal, M.K.; Mallik, M. Densification Behavior of ZrB₂–MoSi₂–SiC_w Composite Processed by Multi Stage Spark Plasma Sintering. *Ceram. Int.* 2021, 47, 31948–31972. [CrossRef]
- 44. Monteverde, F.; Grohsmeyer, R.J.; Stanfield, A.D.; Hilmas, G.E.; Fahrenholtz, W.G. Densification Behavior of ZrB₂-MoSi₂ Ceramics: The Formation and Evolution of Core-Shell Solid Solution Structures. *J. Alloys Compd.* **2019**, 779, 950–961. [CrossRef]
- Sciti, D.; Monteverde, F.; Guicciardi, S.; Pezzotti, G.; Bellosi, A. Microstructure and Mechanical Properties of ZrB₂–MoSi₂ Ceramic Composites Produced by Different Sintering Techniques. *Mater. Sci. Eng. A* 2006, 434, 303–309. [CrossRef]
- 46. Hu, D.-L.; Gu, H.; Zou, J.; Zheng, Q.; Zhang, G.-J. Core–rim Structure, Bi-Solubility and a Hierarchical Phase Relationship in Hot-Pressed ZrB₂–SiC–MC Ceramics (M = Nb, Hf, Ta, W). *J. Mater.* **2021**, *7*, 69–79. [CrossRef]
- Rabiezadeh, A.; Hadian, A.M.; Ataie, A. Synthesis and Sintering of TiB₂ Nanoparticles. *Ceram. Int.* 2014, 40, 15775–15782. [CrossRef]
- 48. Mashhadi, M.; Shambuli, M.; Safi, S. Effect of MoSi₂ Addition and Particle Size of SiC on Pressureless Sintering Behavior and Mechanical Properties of ZrB₂–SiC–MoSi₂ Composites. *J. Mater. Res. Technol.* **2016**, *5*, 200–205. [CrossRef]
- 49. Silvestroni, L.; Failla, S.; Neshpor, I.; Grigoriev, O. Method to Improve the Oxidation Resistance of ZrB₂ -Based Ceramics for Reusable Space Systems. *J. Eur. Ceram. Soc.* **2018**, *38*, 2467–2476. [CrossRef]
- 50. Suri, A.K.; Krishnamurthy, N.; Subramanian, C. Issues in the Synthesis and Fabrication of Refractory Carbides, Borides, Silicides and Their Mixtures. *Ceram. Eng. Sci. Proc.* **2010**, *30*, 69–80.
- 51. Dasgupta, T.; Etourneau, J.; Chevalier, B.; Matar, S.F.; Umarji, A.M. Structural, Thermal, and Electrical Properties of CrSi₂. J. Appl. Phys. **2008**, 103, 113516. [CrossRef]
- Rosenkranz, R.; Frommeyer, G. Microstructures and Properties of the Refractory Compounds TiSi₂ and ZrSi₂. Int. J. Mater. Res. 1992, 83, 685–689. [CrossRef]
- 53. Jeng, Y.-L.; Lavernia, E.J. Processing of Molybdenum Disilicide. J. Mater. Sci. 1994, 29, 2557–2571. [CrossRef]
- 54. Nakano, T.; Hagihara, K.; Nakai, Y.; Umakoshi, Y. Plastic Deformation Behavior of NbSi₂/MoSi₂ Crystals with Oriented Lamellae. *Intermetallics* **2006**, *14*, 1345–1350. [CrossRef]
- 55. Inui, H.; Moriwaki, M.; Ando, S.; Yamaguchi, M. Plastic Deformation of Single Crystals of CrSi₂ with the C₄₀ Structure. *Mater. Sci. Eng. A* **1997**, 239–240, 63–68. [CrossRef]
- Fu, Z.; Koc, R. Microstructure and Mechanical Properties of Hot Pressed Submicron TiB₂ Powders. *Ceram. Int.* 2018, 44, 9995–9999. [CrossRef]

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