metals

Article

Self-Propagating High Temperature Synthesis of TiB_2–$MgAl_2O_4$ Composites

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Abstract: Metal borides are widely used as heat-insulating materials, however, the range of their application in high-temperature conditions with oxidative medium is significantly restricted. To improve the thermal stability of structural materials based on titanium boride, and to prevent the growth of TiB_2 crystals, additives based on alumina-magnesia spinel with chemical resistant and refractory properties have been used. The aim of this work is to study the structure of TiB_2 with alumina-magnesia spinel additives obtained by self-propagating high-temperature synthesis (SHS). TiB_2 structure with uniform fine-grained distribution was obtained in an $MgAl_2O_4$ matrix. The material composition was confirmed by X-ray diffraction analysis (DRON-3M, filtered Co kα-emission), FTIR spectroscopy (Thermo Electron Nicolet 5700, within the range of 1300–400 cm^{-1}), and scanning electron microscopy (Philips SEM 515). The obtained material represents a composite, where the particles of TiB_2 with a size of 5 µm are uniformly distributed in the alloy of alumina-magnesia spinel.

Keywords: titanium diboride; alumina-magnesia spinel; self-propagating high-temperature synthesis; composites

1. Introduction

Self-propagating high-temperature synthesis (SHS) is used to develop new technologies for the production of refractory nonmetallic composite materials with defined properties. In spite of the fact that metal carbides and borides are widely used as insulation materials, the range of their application in oxidative mediums at high temperatures is very restricted. To increase the refractory properties of metal carbides and borides, alumina-magnesia spinel $MgAl_2O_4$ with the melting temperature of 2105 °C, which corresponds to the high level of refractoriness [1], is used as an additive.

Magnesium and aluminothermic synthesis is widely used for the production of refractory ceramic materials, e.g., with the use of metallothermic reduction in a TiO_2–MgO–Al_2O_3–Al system, the refractory materials based on $MgAl_2O_4$ and titanium carbonitrides are obtained [2]. High-strength porous ceramic material, containing in its composition $MgAl_2O_4$, TiB_2, TiO_2, $Al_4B_2O_6$, and $Mg_2B_2O_5$ was obtained in a TiO_2–B_2O_3–Al system with MgO additives. This material can be used as a catalyst at temperatures of 600 °C–700 °C in an open atmosphere [3]. Moreover, aluminum is widely used in the synthesis of composite materials. In the structure of composites, the intermetallic matrices from both TiAl/Ti_3Al and $MgAl_2O_4$ are incorporated [4]. In all of the abovementioned works, $MgAl_2O_4$ is synthesized in the form of particles.

Another method of heat-resistant composite production is through titanium diboride synthesis from its elements with the use of chemical-resistant and refractory alumina-magnesia spinel ($MgAl_2O_4$). This method allows decelerating high-temperature solid-phase oxidative reactions in the process of material exploitation.

The aim of this work is to study the phase composition and microstructure of a TiB_2 + $MgAl_2O_4$ heat-resistant composite obtained by self-propagating high-temperature synthesis with $MgAl_2O_4$ additives of different concentrations.

At high temperatures (~3000 °C), spinel melts and spreads along the surface of TiB_2 grains, forming the matrix that protects the TiB_2 grain surface with the spinel.

2. Materials and Methods

To prepare reaction mixtures, dried in a vacuum at temperature of 200 °C for 2 h, titanium powders (TPP-8, JSC "Avisma"; titanium composition ~96 wt %; particle size < 160 μm), amorphous boron (B-99A-TU-6-02-585-75), and alumina-magnesia spinel (TU 6-09-01-136) were used. Four mixtures of different compositions were prepared: (1) 90% (Ti + 2B) + 10% $MgAl_2O_4$; (2) 75% (Ti + 2B) + 25% $MgAl_2O_4$; (3) 60% (Ti + 2B) + 40% $MgAl_2O_4$; (4) 50% (Ti + 2B) + 50% $MgAl_2O_4$. Powders were thoroughly mixed to obtain homogenous blends. Then, from the obtained mixtures, porous (40–45%) cylindrical particles were formed with a diameter of 20 mm and a length of 30–32 mm by using a hydraulic press. Self-propagating high-temperature synthesis was conducted in a constant pressure setup in argon atmosphere at a pressure of ~6 atm. Samples ignition was carried out using an ignition mixture of powders (Ti + 2B) with the help of a tungsten filament, which was supplied with a short-term electrical impulse. The maximal combustion temperature was detected by the tungsten-rhenium thermocouple BP5-BP20 with a diameter of 100 μm. Temperature registration was conducted with the use of an analog-to-digital converter LA-20USB connected with a personal computer.

The compositions of the obtained materials were proved by X-ray phase analyses (Dron-3M, filtered Co kα-emission, Saint Petersburg, Russia), IR spectroscopy (FTIR spectrometer Nicolet-5700, Thermo Electron Corporation, Atkinson, USA). Measurements were carried out using an add-in device of scattering reflection in KBr at a frequency interval of 1300–400 cm^{-1}. To study the microstructure, an optical microscope (Axiovert 200M, OM, Karl Zeiss, Germany) and a scanning electron microscope (SEM-515, Philips, Amsterdam, The Netherlands) were used.

3. Results and Discussion

Among gas-free systems, the Ti-B system is characterized by the highest exothermicity. For a powder mixture with the ratio of components Ti:B = 1:2 the adiabatic temperature of combustion is Tad = 3190 K [5]. Alumina-magnesia spinel $MgAl_2O_4$ is inert in relation to the mixture Ti-2B. In Table 1, the physicochemical properties of spinel are presented [6,7].

Table 1. Physicochemical properties of compounds.

Compound	Melting Temperature, °C	Density, g/cm³	$-\Delta H^\circ_{form}$, kJ/mol
$MgAl_2O_4$	2135	3.8	2307.8
TiB_2	2850	4.45–4.50	293.3
$MgTiO_3$	1680	3.91	1573.6
α–Al_2O_3	2045	3.99	1675.0

Figure 1 shows the combustion thermogram of the TiB_2 (75 wt %) + $MgAl_2O_4$ (25 wt %) system. The maximal combustion temperature is 2300 °C, which is higher than the spinel melting temperature. Synthesis was conducted layer-by-layer in the steady state combustion conditions. Similar combusting conditions were observed for Ti + 2B + *x*Cu and Ti + 2B + *x*Fe systems. Depending on their content, different metal alloys partially or fully surround particles of titanium borides [8,9].

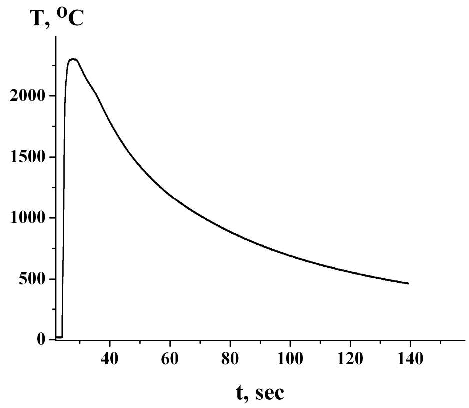
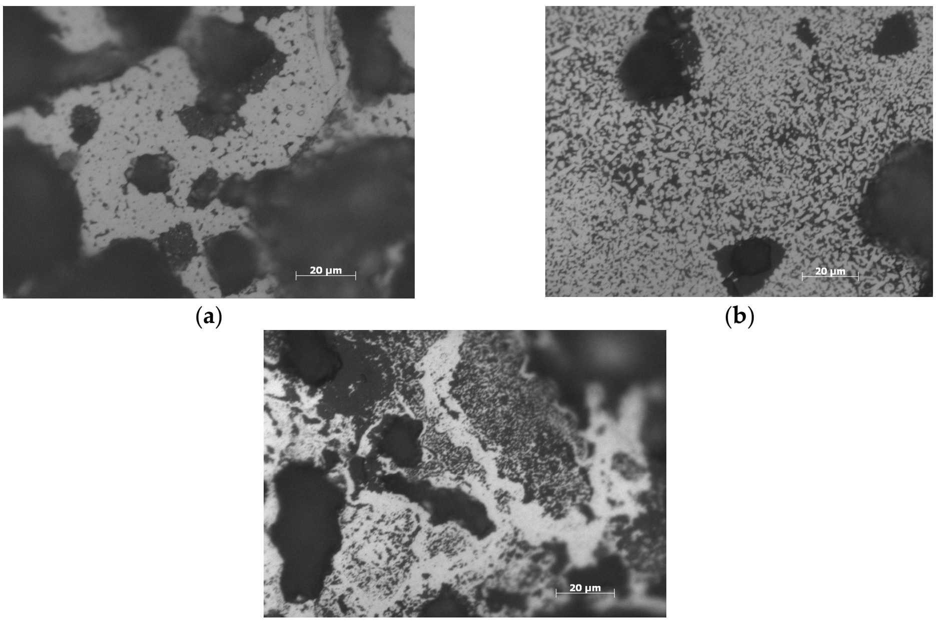


Figure 1. Combustion thermogram of the TiB_2 (75 wt %) + $MgAl_2O_4$ (25 wt %) system.

Studies on the microstructure of the composite blends based on TiB_2 with different $MgAl_2O_4$ compositions showed that, depending on the amount of added spinel, the composite structure change (Figure 2). If the amount of added $MgAl_2O_4$ is <10%, the grains of titanium diboride in the microstructure of the composite are partially surrounded by a solidified alloy of $MgAl_2O_4$ (Figure 2a). The best results were obtained at a spinel composition of 25%. The fine-grain microstructure from TiB_2 grains (light crystals) was observed, which is fully surrounded by spinel (dark areas). When 40% $MgAl_2O_4$ was added to the blend during the synthesis, the formation of a non-homogeneous structure was observed. The structure contains areas with the fine-grained titanium diboride and adjusting areas from alumina-magnesia spinel (Figure 2c).



(**a**) (**b**) (**c**)

Figure 2. Microstructure of SHS composites based on titanium diboride with additions of $MgAl_2O_4$: (**a**) 90% (Ti + 2B) + 10% $MgAl_2O_4$; (**b**) 75% (Ti + 2B) + 25% $MgAl_2O_4$; (**c**) 60% (Ti + 2B) + 40% $MgAl_2O_4$.

When 45% $MgAl_2O_4$ is added to the composite, the mixture does not burn in this case, because $MgAl_2O_4$ is inert.

Complete information on the structure of the product formed during SHS can be obtained by analyses of fracture surfaces, studied with scanning electron microscopy. Figure 3 shows the microstructure of fractures of SHS ceramic samples based on titanium diboride with the addition of 25% $MgAl_2O_4$ (Figure 3a,b), and 0% $MgAl_2O_4$ (Figure 3c,d).

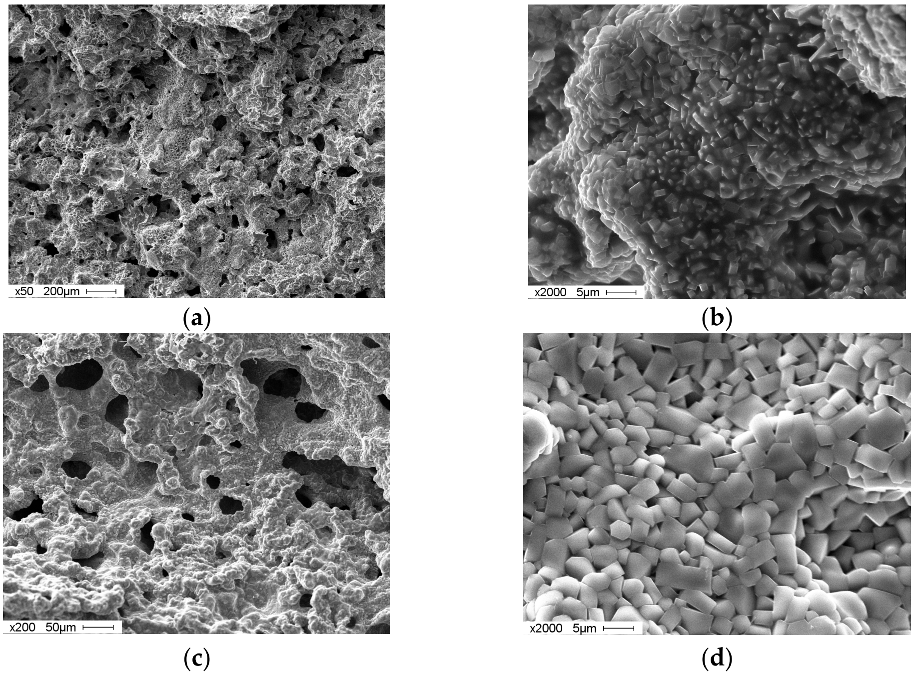


Figure 3. Fractures of SHS samples: (**a**,**b**) 75% (Ti + 2B) + 25% $MgAl_2O_4$; (**c**,**d**) (Ti + 2B).

As can be seen from Figure 3, the addition of 25% $MgAl_2O_4$ leads to the decreasing of TiB_2 crystals (~2 μm), which are surrounded by a solidified alloy of alumina-magnesia spinel. The microstructure of the SHS sample with Ti + 2B composition is formed by large TiB_2 faceted crystals.

Figure 4 shows the diffraction patterns of TiB_2 composites with different amounts of spinel. X-ray diffraction analyses showed that in the composition of alumina-magnesia spinel, there is 12 wt % of $MgAl_2O_4$. Figure 4 shows that spinel is identified in the composite containing 25 wt % of $MgAl_2O_4$, though, metallographically the spinel is identified at 10 wt % of $MgAl_2O_4$.

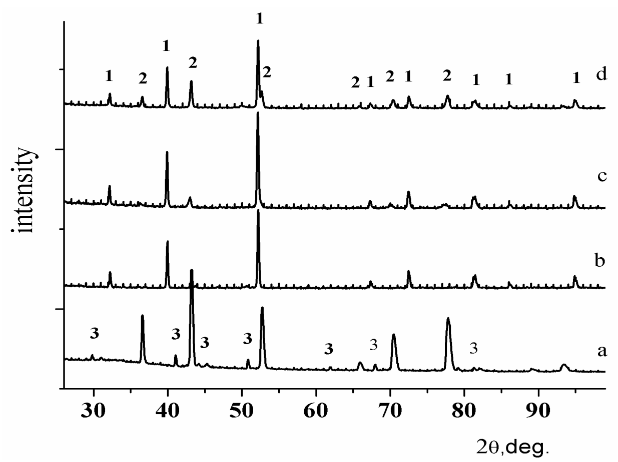


Figure 4. X-ray diffraction patterns of TiB_2 composites with different contents of alumina-magnesia spinel: (**a**) $MgAl_2O_4$; (**b**) TiB_2 + 10% $MgAl_2O_4$; (**c**) TiB_2 + 25% $MgAl_2O_4$; (**d**) TiB_2 + 40% $MgAl_2O_4$. 1-TiB_2, 2-$MgAl_2O_4$, 3-Al_2O_3.

The composite with the fine-grained microstructure containing 25 wt % of $MgAl_2O_4$ was studied by FTIR spectroscopy. Figure 5 shows the FTIR spectrum of $MgAl_2O_4$, TiB_2–$MgAl_2O_4$ composite, corundum, and TiB_2.

Figure 5 (pattern 1) shows that alumina-magnesia spinel has two different absorption bands with maximums at 692.0 cm^{-1} and 540.0 cm^{-1}, related to the tetrahedral coordinated magnesium MgO_4 and octahedral coordinated aluminum of AlO_6. The small peak in the frequency range of 800–900 cm^{-1} proves the presence of Al_2O_3 in spinel content. Irregularity of the spinel structure leading to a change of binding force in the cation sub-lattice is identified by the emergence of an absorption band at 558.7 cm^{-1} [10].

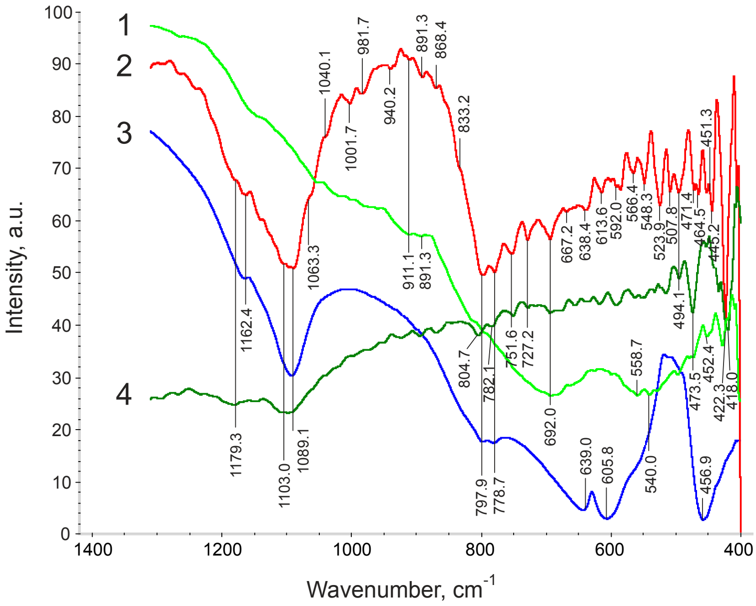


Figure 5. FTIR spectrum in the frequency range of 400–1300 cm^{-1}: (**1**) $MgAl_2O_4$; (**2**) TiB_2 composite 25 wt % of $MgAl_2O_4$; (**3**) gray corundum; (**4**) TiB_2.

FTIR spectrum of composite (TiB_2 + 25 wt % of $MgAl_2O_4$) consists of numerous absorption bands typical for titanium diboride, spinel, and corundum (pattern 2).

According to the burning thermogram for the 75 wt % TiB_2 + 25 wt % $MgAl_2O_4$ system, the burning temperature is 2300 °C. Therefore, $MgAl_2O_4$ is partially decomposed with corundum formation.

$$MgAl_2O_4 \xrightarrow{T} Al_2O_3 + MgO$$

Pattern 3 shows the FTIR spectrum of gray corundum. Along with absorption bands at 639.0 cm^{-1}, 605.8 cm^{-1}, and 456.9 cm^{-1} typical for octahedral coordinated aluminum AlO_6 in α–Al_2O_3, there are absorption bands at 1089.1 cm^{-1}, 797.9 cm^{-1}, and 778.7 cm^{-1}, related to the tetrahedral coordinated aluminum AlO_4 [11]. The same absorption bands are observed in the composite spectrum.

It is well known that α–Al_2O_3 contains aluminum atoms which are octahedrally coordinated by oxygen [10,12]. According to the literature data [13], the gray color of corundum is caused by the presence of aluminous spinel $AlOAl_2O_3$. This spinel was identified during the electrocorundum synthesis in reducing medium [13]. The melting temperature of spinel is 1980 °C [1].

At the interference level, the absorption bands at 940.2 cm^{-1}, 727.2 cm^{-1}, and 507.8 cm^{-1} are observed. They can be referred to $MgTiO_3$ [12]. The formation of $MgTiO_3$ is possible during the synthesis at the phase boundary between TiB_2 and $MgAl_2O_4$.

Oxygen and MgO can be borrowed during the thermal decomposition of spinel. In this case, aluminum is moved from an octahedral coordination to a tetrahedral one with the formation of both $MgTiO_3$ and aluminous spinel with an intensive absorption band at 1089.1 cm^{-1}. It is well-known [14] that at high temperatures over Al_2O_3, the gas phase is formed as a result of thermal dissociation. The gas phase contains aluminum sub-oxides Al_2O and AlO^-.

$$Al_2O_3 \xrightarrow{T} Al_2O \uparrow + O_2 \uparrow$$

Aluminum sub-oxides can also participate in the formation of aluminous spinel $AlOAl_2O_3$.

$$2Al_2O_3 + Al_2O + O \rightarrow 2AlOAl_2O_3$$

The FTIR spectrum of this composite (pattern 2) represents the envelope line along the spectrum of alumina-magnesia spinel. The overlap of numerous bond oscillation frequencies, related to the TiB_2, corundum, aluminous spinel, and $MgTiO_3$, is observed.

Studies showed that the obtained composite consists of TiB_2 fine grains, which are homogeneously distributed in the alumina-magnesia matrix containing α–Al_2O_3. Traces of $MgTiO_3$ and aluminous spinel are also present in the composite.

According to the literature data [5], 12 mol % of MgO and 85.5 mol % of Al_2O_3 can be dissolved in alumina-magnesia spinel. In Table 2, the eutectic melting temperatures in the MgO–Al_2O_3 system are presented.

Table 2. Eutectic melting temperatures in the MgO–Al_2O_3 system.

Chemical Compounds in Eutectics	Al_2O_3 Composition, wt %	Melting Temperature, °C
MgO, $MgAl_2O_4$	55	1995
$MgAl_2O_4$, Al_2O_3	98	1920

Melting temperatures of TiB_2, α–Al_2O_3, $MgTiO_3$, and $MgAl_2O_4$ as well as their eutectics are presented in Tables 1 and 2. As can be seen from Table 2, all values of the melting temperatures are very high, which proves that the obtained ceramic material is refractory.

4. Conclusions

It was shown that structure with a homogeneous fine-grained distribution of TiB_2 grains was obtained by using 25 wt % of $MgAl_2O_4$.

The formed surface layer of $MgAl_2O_4$ on the grains boundary of TiB_2 serves as a blocking protection from titanium diboride oxidation and prevents the growth of TiB_2 crystals.

A partial decomposition of spinel occurred during the composite synthesis. This is proved by the presence of $MgTiO_3$ and corundum traces in the composite, which were identified by FTIR spectroscopy.

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Author Contributions: Nina Radishevskaya performed FTIR-spectroscopy experiments and analyzed the data; Olga Lepakova conducted the microstructure research of samples; Natalia Karakchieva conducted the X-ray phase analyses of samples; Anastasiya Nazarova conducted the synthesis of samples; Nikolai Afanasiev wrote the paper; Anna Godymchuk and Alexander Gusev studied SHS characteristics, such as combustion temperature and combustion wave propagation mode and velocity.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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