

Formation of Diamond-like Carbon Using Self-Propagating High-temperature Synthesis

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Abstract

Carbon was detected in magnesium aluminate spinel (MAS) prepared by self-propagating high-temperature synthesis (SHS). Periclase MgO, alumina Al_2O_3 , fuel Al powder, 2 wt% boron, and oxidizer $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as starting reactants for MAS synthesis. The phase composition, structure, and surface morphology of the samples were studied. Gases evolved during combustion were analyzed. IR spectroscopy shows that the carbon in the synthesized product has a diamond-like structure that is similar to detonation diamonds. Cascade parallel and consecutive exothermic reactions cause an increase in temperature. The initial components are impregnated with melts of boron oxide and metallic aluminum and saturated with the evolved gases during fast synthesis. The rapid growth of spinel crystals and cavitation occurring in a dynamically changing system create high pressure. All this triggers the proton-boron reaction with the formation of carbon. Possible mechanisms for the formation of carbon in the synthesized products are suggested on the basis of the experimental data.

Keywords: self-propagating high-temperature synthesis, spinel, parallel and consecutive reactions, carbon, Low-Energy Nuclear Reaction.

1. Introduction

Diamond is an allotrope of carbon. Due to sp^3 hybridization of orbitals, each carbon atom in a diamond forms equally strong σ -bonds with four neighboring atoms, ensuring its exceptional hardness. Diamonds have a wide and diverse range of applications due to their high refractive index ($n \sim 2.417$) and high thermal conductivity ($\lambda = 900 \div 2300 \text{ W/m}\cdot\text{K}$). They are used in cutting tools, jewelry, and the aerospace industry. An example is the Pioneer station launched in 1978 to study Venus. To quickly remove extreme temperatures, the aircraft surface was coated with synthetic diamonds. Even tiny crystals allow several frequency signals of different frequencies to pass through a single cable, which is highly resistant to temperature fluctuations and voltage surges. American scientists from Stanford University and SLAC National Accelerator Laboratory

(U.S. Department of Energy) have learned to produce diamond-insulated nanowires with a conductive center three atoms in diameter [1]. Synthetic diamond is used in high-precision telescope optics at the world's leading observatories, as well as in laser devices.

There are several methods for producing synthetic diamonds. Currently, due to its relatively low cost, the HPHT (high-pressure high-temperature) method is the most common method for mass production of diamonds. Multi-ton presses are used to apply pressures up to 5 GPa and temperatures up to 1500 °C. A capsule containing carbon, solvent metal, and diamond seed attached to the bottom is placed in a press, pressurized, and heated to above 1400 °C. The metal melts, dissolving the carbon and allowing carbon atoms to move towards the seed, thereby forming large diamonds. The HPHT method uses three types of presses: belt, cubic and split sphere. One of the most compact, cost-effective and efficient diamond growing machines is a Split-Sphere High Pressure Apparatus (BARS). It was developed in 1989-1991 by scientists of the Sobolev Institute of Geology and Mineralogy (Siberian Branch of RAS) [2-5].

Chemical vapor deposition (CVD) is another method to produce synthetic diamonds. Diamond growth occurs through the deposition of carbon atoms from hydrogen-carbon plasma onto a seed crystal substrate. The growth process is performed at pressures below 27 kPa. This method is popular in laboratories. By growing diamonds from the gas phase, it is possible to precisely control the chemical composition of inclusions in the product and to produce large-area diamond films [6-8].

The third method involves forming nanodiamonds by a shock wave from explosives in a sealed metal chamber. During the explosion, high pressures and high temperatures transform carbon from carbon-containing explosive into diamond. The transformation of carbon into the diamond phase occurs in a detonation wave. After the explosion the condensed products of explosive transformation, including diamonds, are extracted and purified from impurities. This method is intended to produce diamond powders used as abrasives. The major producers are Russia, Belarus and China [9-14].

One more method for producing micron-sized diamond crystals is based on processing graphite with high-power ultrasound. This method has been demonstrated in laboratory conditions, but has not yet found commercial success.

Scientists from Germany and the USA also produced nanodiamonds from plastic bottles in laboratory conditions. They were inspired by “diamond rains” on Neptune and Uranus. Diamonds on these planets are formed under the influence of extremely high pressure and temperatures with the participation of oxygen and hydrocarbon gas [15]. Scientists from Stanford University synthesized diamond from hydrogen and carbon molecules in diamondoid powders found in crude oil and natural gas. The synthesis was performed in a hyperbaric chamber (diamond anvil cell), which can generate pressures comparable to those at great depths in the Earth’s crust. Samples were heated to high temperatures with a laser. It has been found that triamantane (a three-component diamondoid) can transform into diamond. At 900 K and 20 GPa, carbon atoms align and hydrogen dissipates. The transformation occurs in fractions of a second. A small sample placed inside the cell makes it impossible to produce diamonds on an industrial scale. However, these studies provide key insights into the processes involved in diamond synthesis [16].

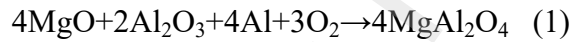
We found diamond-like carbon in magnesium aluminate spinel (MgAl_2O_4) prepared by self-propagating high-temperature synthesis (SHS) in the $\text{MgO-Al}_2\text{O}_3\text{-Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O-Al}$ system with boron additives. It has been shown previously [17] that as the concentration of boron used as an energy additive in the starting mixture rises, the amount of carbon in the product also increases. Due to the chemical inertness of MgAl_2O_4 at high temperatures, the carbon formed during the boron-proton reaction is retained in pores and intergranular space of the spinel. Gromov A.A. [18] reported the possibility of low-energy nuclear reactions in SHS processes, where calcium was detected in the products synthesized by the aluminothermic reaction of aluminum with iron oxide Fe_2O_3 . Vysotsky V.I. [19, 20] proposed a theoretical justification for low-energy nuclear reactions at room temperature. The formation of by-products at temperatures up to 3000 °C, which are

neither contained in the initial substances nor formed in chemical reactions, has not been sufficiently studied experimentally.

The purpose of this work is to determine the mechanism of carbon formation in magnesium aluminate spinel prepared by SHS in the $\text{MgO-Al}_2\text{O}_3\text{-Mg(NO}_3)_2\cdot 6\text{H}_2\text{O-Al}$ system with boron additives.

2. Materials and methods

The composition of the starting mixture for synthesizing magnesium aluminate spinel was calculated using the equation:



Powders of aluminum oxide Al_2O_3 (98%, $d=0.3\text{-}3\ \mu\text{m}$) and magnesium MgO (98.67%, $d=3.5\text{-}10\ \mu\text{m}$) were used for preparing reaction mixtures. Aluminum powder (ASD-4) with a dispersity $\leq 30\ \mu\text{m}$ was used as a fuel. Magnesium nitrate hexahydrate $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ was added as an oxidizer. To increase the thermal stability of the system, 2 wt.% amorphous boron with a particle size of $1\text{-}5\ \mu\text{m}$ was added with a B:Al=1:3.6 ratio. The prepared mixture was thoroughly ground in an agate mortar until a homogeneous mass was formed. Pressed cylinders with a height of 33-35 mm, a diameter of 20 mm, and a porosity of 45-47% were prepared by pressing the starting powder mixtures in the cylindrical molds. The porosity was determined according to the formula:

$$\eta = \left[1 - \left(\sum_{i=1}^n \frac{m_i}{\rho_i} / 2\pi r^2 h \right) \right] \times 100\%$$

where ρ_i is the density of the i -th component (compact), kg/m^3 ; r is the sample radius, m; m_i is the mass of the i -th component, kg; h is the sample height, m; n is the number of components in the mixture.

The spinel was synthesized by the SHS method in the air at atmospheric pressure. Layer-by-layer combustion was performed in a gradient resistance furnace (Fig. 1).

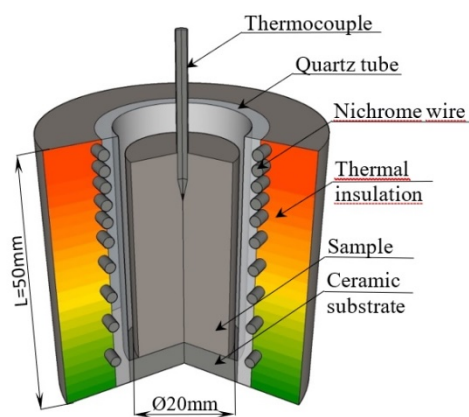


Fig. 1 Schematic of the experimental setup for spinel synthesis by the SHS method.

Cylindrical samples were placed in the center of the furnace, the inner part of which included a quartz tube with a diameter of 25 mm. Ignition occurred in the upper part of the sample, where the temperature was maximum. The combustion wave, observed visually, propagated from top to bottom. Combustion of the sample occurred within a few seconds. During SHS synthesis of the spinel, temperature-time profiles were measured using a tungsten-rhenium thermocouple (BP5/BP20, 100 μm in diameter) placed in the center of the upper part of the samples. Data were recorded using an analogue-digital converter (LA-20USB) connected to a PC.

The synthesized products were ground in an agate mortar for structural analysis. Starting and synthesized products were identified by X-ray diffraction (XRD) using a diffractometer (Shimadzu XRD6000, filtered $\text{CoK}\alpha$ radiation). Concentrations of oxygen, nitrogen and hydrogen in amorphous boron were determined using an elemental analyzer (LECO ONH836). Structural features were studied by infrared spectroscopy (Nicolet 5700 FTIR spectrometer) in KBr. Spectra were obtained in the range of 4000-400 cm^{-1} using a diffuse reflectance spectrometer with a resolution of 4 cm^{-1} .

The surface morphology and elemental composition of the synthesized products were studied using a scanning electron microscope (Philips SEM 515) equipped with EDAX (local micro-X-ray spectral analysis system) with a detection limit of 0.2 wt.%. To improve the contrast

of the images, a 0.05 μm thick silver film was deposited on the surface of the samples. The microstructure of the final products was studied by optical microscopy (Axiovert 200M).

The carbon concentration in the starting components was determined by an analyzer (AN-7529). The sample was burned in a stream of oxygen in a tube furnace at 1250°C for automatic coulometric determination of the carbon dioxide formed during combustion.

Gases emissions during the combustion of mixtures were recorded in the optical range of $\lambda=200\text{-}1100\text{ nm}$ by a spectrometer (Ocean Optics HR4000CG-UV-NIR) through a quartz fiber-optic cable (QP400-2-SR-BX). Spectra were interpreted using the Ocean Optics SPECLINE-U database. The temperature of the gases released during the spinel SHS was measured using the spectral pyrometry method described in [21].

3. Experiment and discussion of results

3.1 Spinel synthesis

Aluminum is widely used as a fuel in the production of refractory compounds. High heat release during its oxidation, relative availability and low cost make Al attractive for SHS processes.

SHS of magnesium aluminate spinel in the $\text{MgO-Al}_2\text{O}_3\text{-Mg(NO}_3)_2\cdot 6\text{H}_2\text{O-Al-B}$ system was performed in a gradient resistance furnace in the air at atmospheric pressure in the layer-by-layer combustion mode. Figure 2 shows the temperature-time profiles of SHS of MgAl_2O_4 spinel. The synthesis began with the preheating of the starting mixture, during which the decomposition of magnesium nitrate hexahydrate $2\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ was observed. The mixture of nitrogen oxides, water vapors and oxygen produced from the decomposition of magnesium nitrate hexahydrate is an oxidizing and highly reactive medium, which ensures rapid ignition and better combustion of the samples. The overall equation for the salt decomposition reaction can be represented as follows:



The leading processes responsible for SHS in this system are the oxidation reactions of aluminum and boron. According to the values of enthalpies for aluminum and boron oxidation (Table 1), aluminum should be oxidized first in the SHS process (Table 1), but its oxidation is prevented by a strong oxide film on the surface.

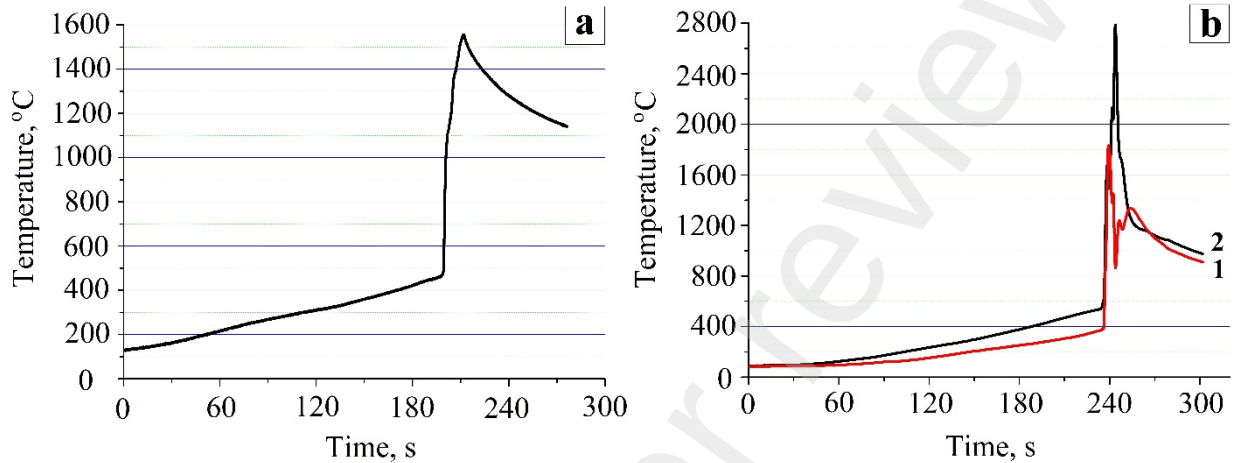
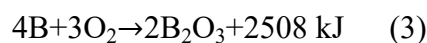


Fig. 2. Temperature-time profile of SHS of magnesium aluminate spinel. Composition of the mixture: MgO , Al_2O_3 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Al and B, where (a) is the normal sample, (b) is the anomalous sample; thermocouple (1) is inside the upper part of the sample and thermocouple (2) is on the end surface of the sample.

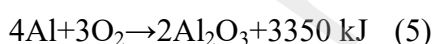
The protective properties of the oxides on the surface of particles were evaluated using Pilling-Badworth coefficients. For aluminum and boron, the coefficients are 1.28 and 2.46, respectively (Table 1). Metals with a value of $1.0 < \beta < 1.5$ have the strongest oxide coating. These metals include aluminum. High coefficients ($\beta > 1.7$) cause cracking in the oxide layer and reduce its protective properties, which is typical for boron [22].

The heat release in the system begins with the oxidation of boron. Boron was added to the starting mixture in an amount of 2 wt.% to increase the thermal stability and reduce the ignition temperature of the mixture.



It is known [17] that fine boron ($\leq 1 \mu\text{m}$) ignites in a humid environment at an initial temperature of 230-530 °C, which agrees well with our experimental data.

Boron plays a dual role. On the one hand, boron is an energy additive (reactions 3 and 4), and on the other hand, boron oxide B_2O_3 , formed by oxidation of boron, acts as a mineralizer, accelerating the synthesis of spinel. For example, the formation of spinelides in production of refractories can be accelerated by 15-20 times by adding 2 wt.% boron oxide B_2O_3 [23]. The oxidation of boron is followed by the oxidation of aluminum, which proceeds through two reactions – aluminothermic reaction and direct oxidation of aluminum:



The ability of elements to donate or accept electrons characterizes their redox properties. Both aluminum and boron have reducing properties. However, the atomic radius of boron is smaller (Table 1) than that of aluminum, so the strength of bond between electrons and the nucleus of boron is higher. Therefore, aluminum will reduce boron from B_2O_3 oxide. The aluminum powder used in the synthesis was taken in a small excess, since at high temperatures, the formation and evaporation of a gas phase containing aluminum and its suboxides, $\text{Al}_2\text{O}_{(g)}$, $\text{AlO}_{(g)}$ and $\text{Al}_{(g)}$, occur [24]. Exothermic reactions are responsible for the self-heating of the mixture, followed by the spinel synthesis with heat release.

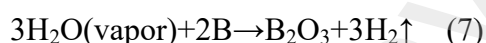


Table 1. Physical and chemical properties of aluminum, boron and their oxides.

Compound	$T_{\text{melt}}, ^\circ\text{C}$	$T_{\text{boil}}, ^\circ\text{C}$	$\Delta H^\circ_{298}, \text{kJ/mol}$	β	E, eV	R^{3+}, nm	R, nm
B	2075	3707	-	2.46	8.298	0.022	0.091
Al	660	2327	-	1.28	5.986	0.051	0.143
B_2O_3	290-450	1860-2100	-1275.3	-	-	-	-
Al_2O_3	2044	2980	-1675.0	-	-	-	-

β is the Pilling-Badworth coefficient, E is ionization energy $\text{E}^0 \rightarrow \text{E}^+$, eV; R^{3+} is the cation radius nm, R is the atomic radius, nm.

As shown in the thermograms, the mixture with 2 wt.% boron has the maximum combustion temperature – 1550 °C (the thermocouple is placed inside the upper part of the sample). The mixture ignites at 465 °C, and the boron oxide produced during the synthesis immediately goes to a molten state (Fig. 2a). The melting and boiling temperatures of aluminum, boron, and their oxides are shown in Table 1. Since aluminum particles are surrounded by a B₂O₃ melt after the oxidation of boron, the aluminothermic reaction will predominate (4). The reaction between boron and water vapor produces hydrogen.



Water is released during reaction (2) and due to the decomposition of boric acid present in the initial boron as an impurity.

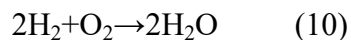


The interaction between water vapor and aluminum also leads to the formation of hydrogen. Due to the difference in the thermal expansion coefficient between Al₂O₃ (8.6·10⁻⁶ deg⁻¹) and Al (33.5·10⁻⁶ deg⁻¹) during rapid heating, the oxide film on aluminum particles cracks and exposed areas of Al appear.



Some samples showed a sharp increase in the maximum synthesis temperature caused by a change of the combustion mode to thermal explosion. Figure 2b shows the temperature-time profile of SHS with an anomalous temperature increase in the MgO-Al₂O₃-Mg(NO₃)₂·6H₂O-Al-B system containing 2 wt.% boron (anomalous sample). The surface of the sample heats up faster and its maximum temperature reaches 2800°C (Fig. 2b, curve 1). Inside the sample, the ignition temperature is 400°C and the maximum temperature reaches 1820°C, which is 270°C higher than the temperature of the standard sample (Figure 2b, curve 2). This type of combustion seems to be related to the shock-wave mode of ignition of gases evolved during synthesis. During rapid heating, the gases produced do not have time to escape from the sample into the atmosphere, accumulating in the intergranular space. If oxygen and hydrogen are in the same cavity at the same

time, an explosive gas can form. Mixtures of hydrogen with oxygen or air are explosive and can detonate. They burn over a wide range of hydrogen concentrations in the air, ranging from 4 to 9 vol.% in mixtures. Such mixtures can ignite at atmospheric pressure.



3.2 Determination of impurities in the initial boron and synthesized products

As found in [17], with an increase in the boron concentration in the starting mixture, the carbon content in the final products also increases, while the concentration of other initial components remains unchanged. This led to the assumption that it was the boron that originally contained carbon. For the synthesis of spinel, we used amorphous boron powder, which was produced by metallothermy method, in particular, by reducing boron oxide with magnesium. Amorphous boron is more reactive than crystalline boron, but its composition is contaminated with various impurities. Although these impurities (MgB_2 , Mg_3B_2 , MgB_6 , MgB_{12}) are separated by acids (hydrochloric, nitric or hydrofluoric) during boron production, there is no complete purification. The difficulty in producing pure boron is associated with acceptor properties of boron. The tendency of boron to complete the sp^2 -configuration to the most stable sp^3 hybridization determines its ability to capture valence electrons of impurities [25].

Initial boron used in the synthesis of spinel was characterized by XRD for a more detailed study. XRD showed that boron contains both amorphous and fine crystalline components (Fig. 3). The X-ray diffraction patterns show broad halo peaks characteristic of the amorphous phase in the substance, as well as narrow lines of tetragonal and rhombohedral boron. The phases of cubic and hexagonal boron oxide B_2O_3 , and boric acid H_3BO_3 with an orthorhombic crystal lattice are detected.

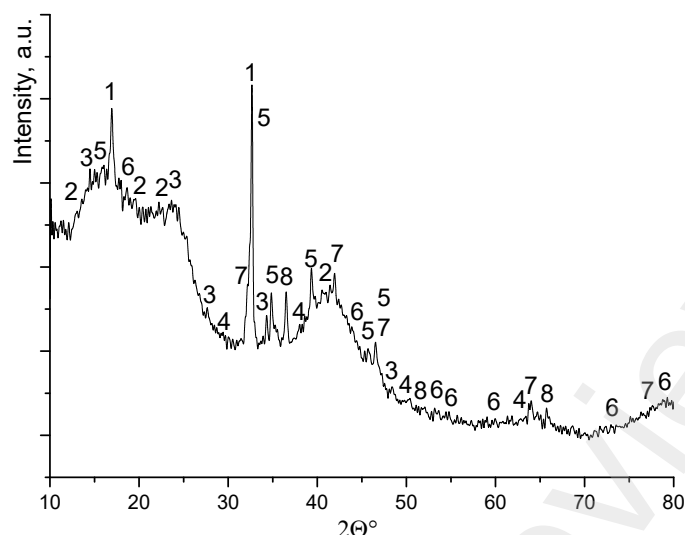
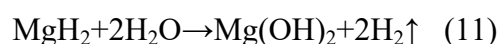
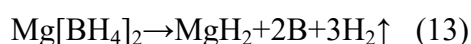


Fig. 3. X-ray diffraction pattern of boron used for the synthesis of magnesium aluminate spinel, where (1) B_2O_3 (Cubic), (2) B (Rhombohedral), (3) B (Tetragonal), (4) B_2O_3 (Hexagonal), (5) H_3BO_3 (Orthorombic), (6) MgB_2H_8 (Tetragonal), (7) MgH_2 (Tetragonal), (8) MgH_2 (Orthorombic).

Tetragonal and orthorhombic magnesium hydride MgH_2 and compound MgB_2H_8 of the tetragonal system were detected as micro-impurities. Impurities of magnesium hydride MgH_2 and magnesium borohydride $Mg[BH_4]_2$, contained in amorphous boron, can release hydrogen when interacting with water [26].



Magnesium borohydride $Mg[BH_4]_2$ melts and decomposes at 305 °C, but begins to sublime already at 230 °C. Noticeable sublimation occurs above 290 °C with the formation of magnesium hydride, boron and hydrogen.



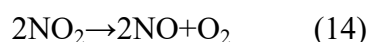
Oxygen and hydrogen-containing impurities in amorphous boron were confirmed by an elemental analysis performed using an elemental analyzer (LECO ONH836). The results of the analysis are presented in Table 2.

Table 2. Concentration of oxygen, nitrogen and hydrogen in amorphous boron

Compound	Oxygen	Nitrogen	Hydrogen
	wt. %		
B-amorphous	2.130±0.01	0.041±0.01	0.378±0.01

The concentration of fixed and adsorbed carbon in the boron used for synthesis was determined by an AH-7529 analyzer. The carbon concentration was $C=0.095\pm0.01$ wt.%. Since only 2 wt.% boron was added to the starting mixture, this concentration of carbon found in the magnesium aluminate spinel samples could not be present in the starting reagents.

X-ray diffraction analysis (Fig. 4) showed that the synthesized magnesium aluminate spinel contained cubic $MgAl_2O_4$ and a small amount of corundum $\alpha-Al_2O_3$ (Rhombohedral). Boron nitride BN (Hexagonal) and carbon micro-impurities of different polymorphic modifications, in particular the Lonsdaleite Hexagonal phase, were detected as noise in XRD patterns. Micro-impurities of Chaoite (Chaoite Hexagonal) were additionally found in the anomalous sample. Diamond (Diamond Cubic) and graphite (Graphite Hexagonal) can also form. The boron nitride micro-impurity, confirmed by infrared spectroscopy, is formed by side reactions with nitrogen oxides:



Nitrogen dioxide produced from magnesium nitrate decomposes into nitrogen monoxide and oxygen at 135-620 °C.

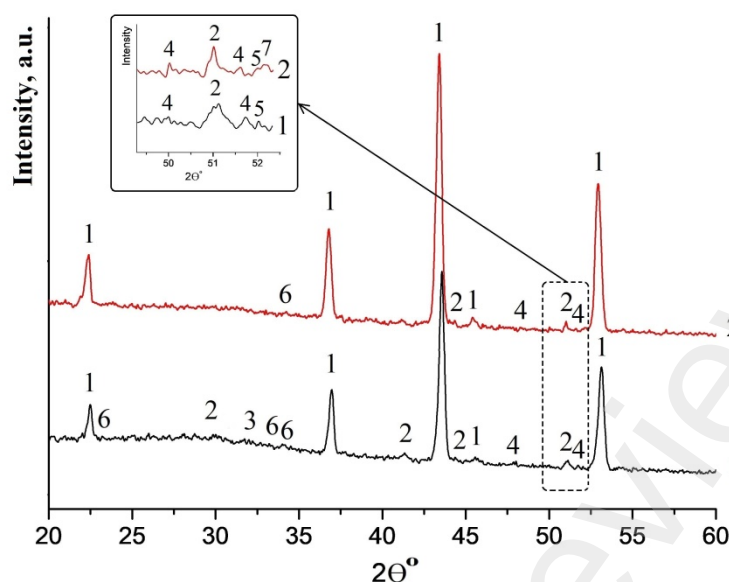


Fig. 4 X-ray diffraction patterns of the magnesium aluminate spinel synthesized in the $\text{MgO-Al}_2\text{O}_3\text{-Al-Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ system with the addition of 2 wt.% boron: (1) anomalous sample, (2) sample with 2 wt.% boron, where (1) is MgAl_2O_4 (Cubic), (2) is $\alpha\text{-Al}_2\text{O}_3$ (Rhombohedral), (3) is BN (Hexagonal), (4) is C-Lonsdaleite (Hexagonal), (5) is C-Diamond (Cubic), (6) is C-Chaoite (Hexagonal), (7) is C-Graphite (Hexagonal).

Lonsdaleite is a hexagonal polymorph of diamond. The mineral lonsdaleite is found in meteorites. It can be produced artificially from graphite at high pressures and temperatures around 900 °C. Lonsdaleite has a diamond-like lattice, which consists of sp^3 -hybridized carbon atoms and differs from diamond in the crystal lattice structure [27]. Chaoite is an exotic mineral, a little harder than graphite. It is formed by impact metamorphism (rock graphite exposed to meteorites). Under laboratory conditions, chaoite was synthesized both under high pressure and in vacuum by heating graphite to 2700-3000 °C.

However, the determination of lonsdaleite, diamond, graphite and chaoite micro phases by XRD is controversial and requires further research.

3.3. Characterization of synthesized products by scanning and optical spectroscopy

Figure 5 shows the surface morphology of the spinel samples with the addition of 2 wt.% boron, examined by scanning electron microscopy (Philips SEM 515). Figures 5a and 5b demonstrate randomly oriented spinel crystals with less distinct, blurred facets, including sheath-shaped skeletal crystals with pores between them. Skeletal crystals are formed under conditions of rapid cooling and are characteristic, for example, of magmatic melts [28].

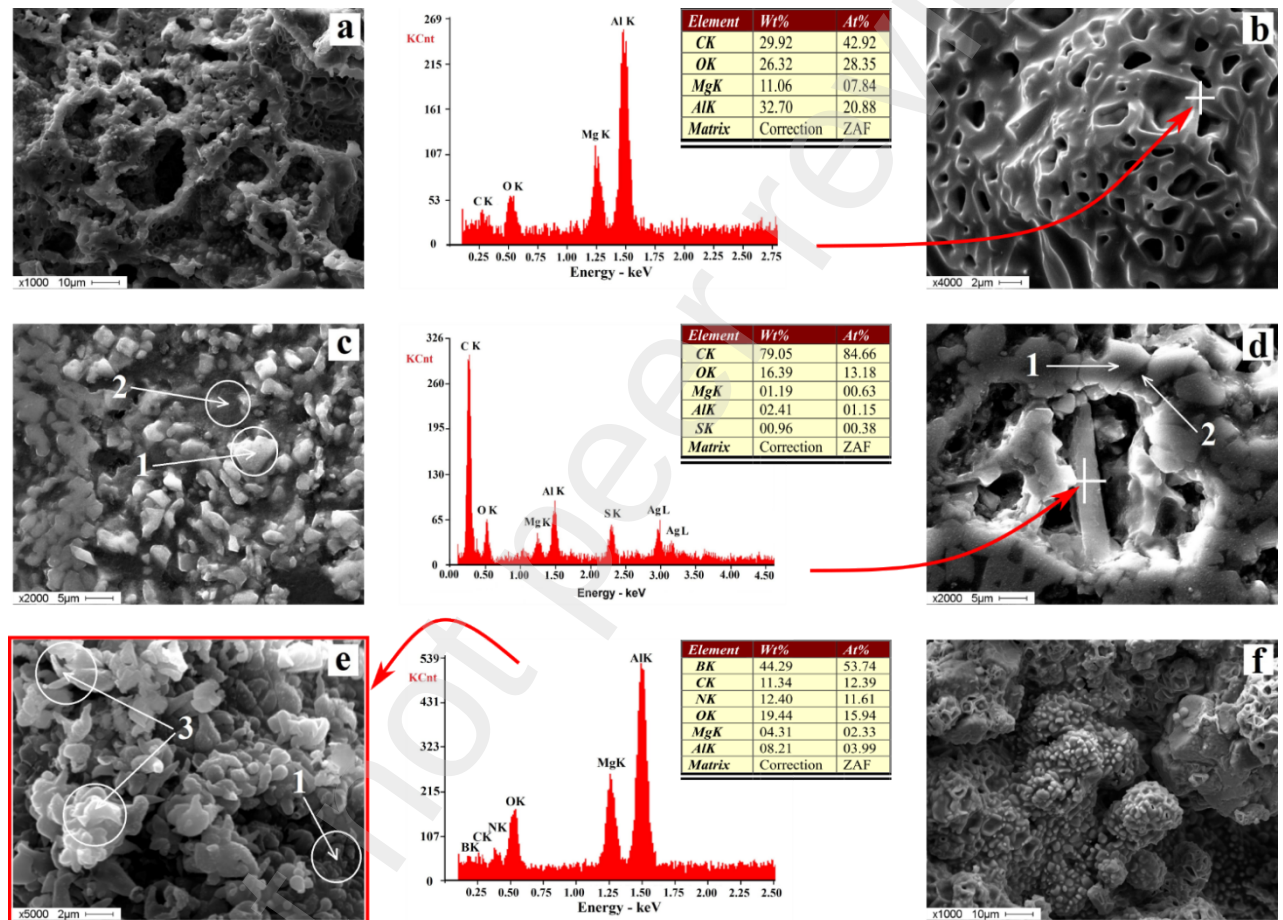
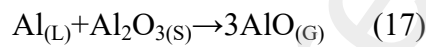
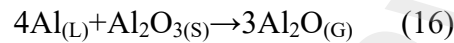


Fig. 5. SEM images and EDS analysis of the spinel samples with the addition of 2 wt.% boron, where (a), (b), (e) and (f) are the cross-sectional view of the sample; (c) and (d) are the cross-sectional view of the anomalous sample. EDS analysis is given for samples (b) and (d) at points marked with a cross, and for the entire sample surface (e); where (1) – MgAl_2O_4 , (2) – C, (3) – BN.

Fig. 6 shows a phase diagram of the $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ oxide system at 1600 °C. Chemical oxide compounds that can be in equilibrium with the oxide melt-liquid are displayed in the diagram.

The MgO-Al₂O₃-B₂O₃ oxide melt is denoted by the symbol L [29]. The molten B₂O₃ is known to dissolve well the oxides of many elements. As can be seen from Fig. 6, the composition of the starting mixture, marked with X (taking into account the oxidation of aluminum and boron to Al₂O₃ and B₂O₃ oxides, and the decomposition of magnesium nitrate hexahydrate to MgO), at 1600 °C falls into the region containing spinel MgAl₂O₄ and liquid oxides.

Along with the liquid phase, gaseous aluminum suboxides are formed during the combustion of aluminum particles:



According to literature data [30], the gas phase above the surface of Al₂O₃ contains aluminum suboxides at 1500-1600 °C.

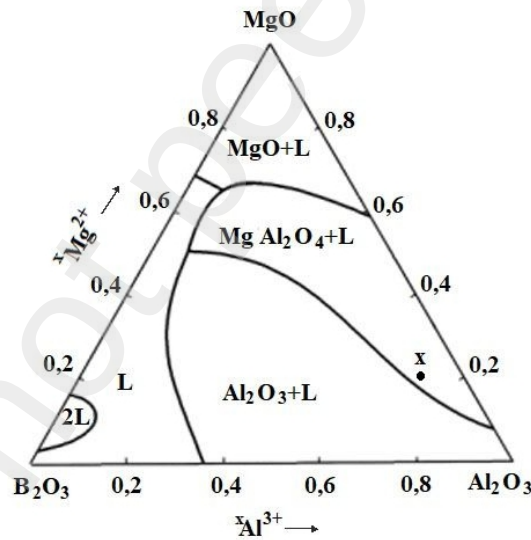


Fig. 6. Composition of the starting mixture (point X) in the ternary phase diagram of the MgO-Al₂O₃-B₂O₃ system at 1600 °C (weight fractions).

Above the Al+Al₂O₃ mixture, the volatility of gaseous components increases significantly (by two orders of magnitude). For example, in the presence of aluminum at 1900 °C, the Al+Al₂O₃ mixture completely volatilizes from the surface of the heating element to form Al₂O_(G), AlO_(G), O,

and $\text{Al}_{(\text{G})}$ [24]. At temperatures of 1800-2000 °C, the volatility of magnesium oxide MgO in a reducing medium is also observed [31].

The sample contains crystals with different structures (normal and skeletal) (Fig. 5f). This indicates different mechanisms of crystal growth. Spinel skeleton crystals form from aluminum suboxides with high heat release. Table 3 shows the enthalpies of formation of aluminum suboxides, most of which have negative values. In addition, the thermal effects of solid-phase spinel synthesis and the reaction of gaseous metastable aluminum suboxides are presented [32].

Table 3. Enthalpies of aluminum suboxide formation and thermal effects of aluminum oxide and spinel MgAl_2O_4 formation reactions

Compound	State of matter	ΔH°_{298} , kJ/mol	Reaction	Q, kJ
MgAl_2O_4	c	-2307.8	$\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4$	31.2
Al_2O	g	-126.4	$\text{MgO} + \text{Al}_2\text{O} + \text{O}_2 \rightarrow \text{MgAl}_2\text{O}_4$	1579.8
AlO	g	+83,7	$\text{MgO} + 2\text{AlO} + \text{O} \rightarrow \text{MgAl}_2\text{O}_4$	2122.9
$(\text{AlO})_2$	g	-406.1	$\text{MgO} + (\text{AlO})_2 + \text{O} \rightarrow \text{MgAl}_2\text{O}_4$	1549.4
AlO_2	g	-184.2	$\text{MgO} + 2\text{AlO}_2 \rightarrow \text{MgAl}_2\text{O}_4 + \text{O}$	1337.8
O	g	+249.3	-	-
MgO	c	-601.6	-	-

Where g is gas, c is solid crystal, Q is the thermal effect of reaction (kJ).

The epitaxial crystal growth occurs when the gas and liquid phases do not have time to enter the reaction zone, and the rapid SHS contributes to this. With an increase in the synthesis temperature, the concentration of volatile gaseous aluminum suboxides and mass transfer through the gas phase increase. Overgrowth of skeleton crystals is observed. The involvement of the liquid phase makes the structures denser. Small amounts of boron nitride are present in both samples. The micrographs in Fig. 5e show hexagonal BN flakes.

The product structure was studied by energy-dispersive X-ray spectrometry (EDS). The study showed that both samples contain Mg, Al, and O, which are characteristic of magnesium aluminate spinel. All samples contain carbon. In the anomalous sample, carbon is detected both in the

intergranular space (Fig. 5c) and in pores as an elongated prismatic crystal embedded in the sample matrix (Fig. 5d). EDS analysis confirms the presence of carbon in the crystal.

The surface of the anomalous sample was examined by optical spectroscopy (Axiovert 200M) (Fig. 7). Numerous crystals were found in the spinel matrix.

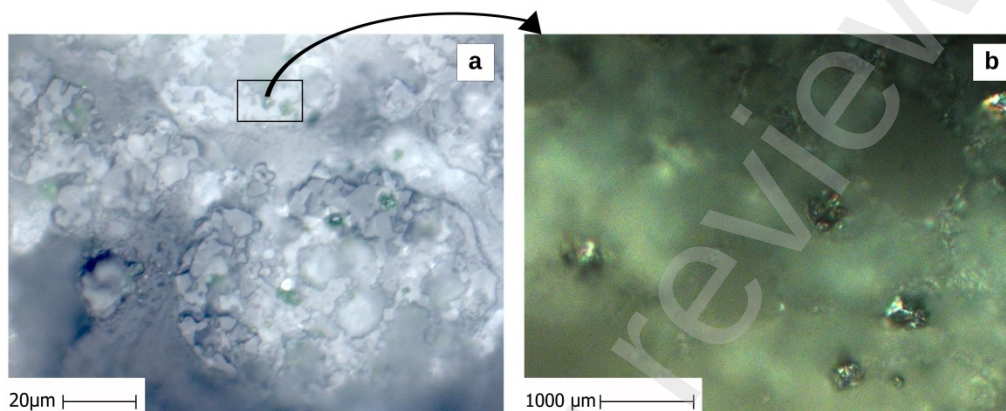


Fig. 7. SEM images (a) of magnesium aluminate spinel produced by SHS with the addition of 2 wt.% boron, where (1) is spinel, (2) is crystals, (3) is pore (epoxy resin); the marked area (b) shows a cross section with the crystals. (Axiovert 200M, DIC (Differential Interference Contrast)).

IR spectroscopy was used to determine a polymorph of carbon found in the samples after SHS.

3.4. IR spectroscopy studies

As shown by IR spectroscopy studies (Fig. 8), the synthesized products contain MgAl_2O_4 . In the spinel structure, tetrahedrally coordinated magnesium $[\text{MgO}_4]$ is visible at 682.8 cm^{-1} . Octahedrally coordinated aluminum $[\text{AlO}_6]$ is observed at 548.9 cm^{-1} . The $\alpha\text{-Al}_2\text{O}_3$ absorption band is detected at $\sim 450.9 \text{ cm}^{-1}$. Boron nitride, present as a micro-impurity, is determined by vibrations of bonds at 1381.0 cm^{-1} , 1359.8 cm^{-1} and 815.3 cm^{-1} , and belongs to hexagonal $\alpha\text{-BN}$ [33]. The presence of boron oxide B_2O_3 in the samples is indicated by the absorption band at 1475.8 cm^{-1} corresponding to asymmetrical valence vibrations of the B-O bond in the planar

triangle $[\text{BO}_3]$, and vibrations of the triangular groups $[\text{BO}_3]$ at 847.5 cm^{-1} [34]. A deformation vibration of the $\delta(\text{OH})$ bond in H-O is observed at 1659.8 cm^{-1} . Detonation diamonds are known to contain microcrystals with defects and a lonsdaleite phase [35, 36]. In our case, the lonsdaleite phase, manifested by an absorption band at 1236.5 cm^{-1} [37], is also detected in the IR spectra of the products. Figure 8 shows the IR spectra of detonation and natural diamonds for comparison.

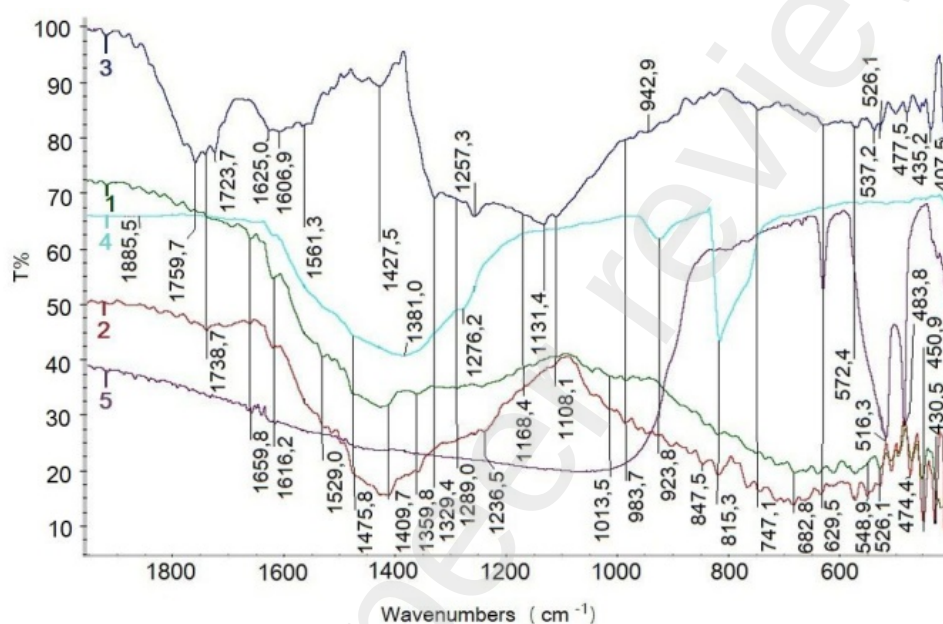


Fig. 8. IR spectra of magnesium aluminate spinel prepared by SHS for the range of $400\text{--}2000 \text{ cm}^{-1}$, where (1) is the product with 2 wt.% B; (2) is the anomalous product; (3) is detonation diamond; (4) is hexagonal boron nitride BN; (5) is natural diamond; (Nicolet 5700 FTIR spectrometer)

The synthesized products exhibit absorption bands characteristic of both detonation and natural diamonds. A broad band in the range of $1329.4\text{--}1108.1 \text{ cm}^{-1}$ of the detonation diamond (UDA-STP), corresponding to vibrations of the diamond lattice bonds, is also observed in the spectrum of carbon in spinel products as a broad shoulder [36, 38, 39]. In contrast to the detonation diamond characterized by isolated single nitrogen atoms (C-centers) as an impurity at 1131.4 cm^{-1} (type Ib diamond), they are almost absent in our samples. However, type Ia diamonds contain aggregated nitrogen at 1289.0 cm^{-1} (A-centers), 1168.4 cm^{-1} , and 1329.4 cm^{-1} (B1-centers) [40]. N atoms are known to move in the lattice and aggregate into groups at high temperatures and

pressures. Thus, A-centers consist of two neighboring nitrogen atoms in the crystal lattice. If two A-centers merge together with a vacancy between them, a B1 center is formed.

A sharp peak in the IR spectrum of the anomalous product in the range of 1409.7-1427.5 cm^{-1} is characteristic of $\nu(\text{CO}_3^{2-})$ carbonate micro-inclusions [41]. It overlaps with the broad band of boron nitride. The absorption bands at 1723.7 cm^{-1} and 1759.7 cm^{-1} are caused by carbonyl ($>\text{C}=\text{O}$) and bridging (C-O-C) groups of carbon oxidation products on the surface of diamond particles. The 1561.3 cm^{-1} band (shoulder) is attributed to a defect with two interstitial carbon atoms in the detonation diamond. Vibrations of graphite bonds can also appear in the range of 1550-1590 cm^{-1} . The detonation diamond exhibits vibrations of graphite deformation bonds at 477.5 cm^{-1} , 436.2 cm^{-1} and 407.5 cm^{-1} . Our samples also contain bonds at 474.4 cm^{-1} and 430.5 cm^{-1} , which can also be attributed to the graphite deformation bonds. However, a slight shift towards lower frequencies of bond vibrations may indicate their weakening. (The values of bond vibrations are lower than those of graphite but higher than those of carbon black). This may be due to non-equilibrium conditions of carbon formation, as well as to the fixation of graphite-like structures on the surface of denser carbon allotropes, such as lonsdaleite or diamond.

The weak 1529.0 cm^{-1} band detected in the spectra is characteristic of B2 defects along $\{100\}$ planes formed by interstitial carbon atoms and partially by nitrogen [42]. Nitrogen in the diamond lattice in the form of lamellar segregations causes absorption in the 1350-1380 cm^{-1} region (B2-centers). The 1359.8 cm^{-1} absorption band indicates inclusions of segregations with a size of 600-1000 Å [43].

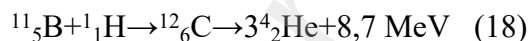
Natural diamond exhibits A-centers at 483.6 cm^{-1} and belongs to the mixed IaA+Ib type. In the range of 900-1080 cm^{-1} , absorption appears in the form of a shoulder, which can be attributed to valence vibrations of $\nu(\text{C-N})$ bonds located on the surface in the crystal lattice of diamonds [44]. Vibrations of $[\text{BO}_4]$ bonds of borates where the boron atom is in tetrahedral coordination can also appear in the range of $\sim 1000\text{-}1100 \text{ cm}^{-1}$ [45]. Infrared spectra of spinel samples with 2 wt.% boron content also show a shoulder in this region. However, it cannot be unambiguously attributed to

CN bond vibrations or [BO4] bond vibrations. The absorption band of natural diamond at 629.5 cm^{-1} is also detected in our synthesized samples.

Thus, carbon formed during rapid SHS has a diamond-like lattice (type Ia) with aggregated nitrogen and carbon defects and may have graphite-like phases and products of carbon oxidation on its surface.

3.5. Mechanism of formation of carbon with a diamond-like lattice

Complex crystallochemical transformations take place in the spinel matrix during nonequilibrium SHS. A proton boron fusion reaction may be a possible way to form a carbon impurity. Proton, merging with the nucleus of boron ^{11}B , forms carbon ^{12}C [46].



The protons involved in the LENR reaction are formed in several ways. They arise at coordinatively unsaturated sites on the surface of aluminum oxide (Lewis acid centers) during the dissociative adsorption of water molecules (Fig. 9). The concentration of these electron-acceptor centers depends on the number of tetrahedrally coordinated Al^{3+} ions in the crystal lattice of aluminum oxide. Figure 9 shows an anion vacancy in Al_2O_3 representing a tetrahedrally coordinated Al^{3+} ion [47].

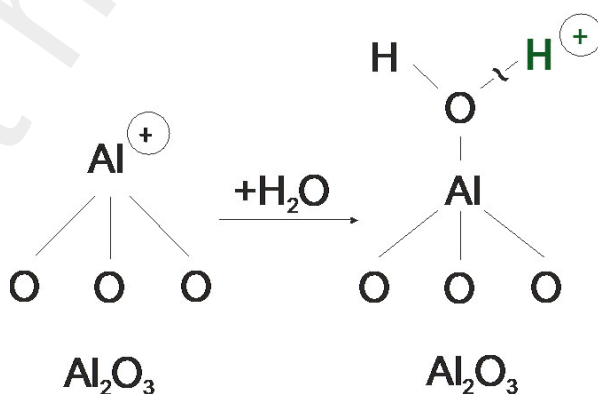
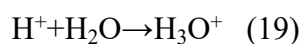


Fig. 9. Proton formation at coordinatively unsaturated sites on the aluminum oxide surface.

The adsorption of water on the surface of aluminum oxide also results in the formation of H_3O^+ hydronium ions.



This bond is formed by the donor-acceptor mechanism. The hydronium ion exists in the gas phase. [48]. In industry, aluminum oxide is widely used as an adsorbent for dehydration of gases and liquids, separation of gas mixtures. Aluminum oxide is used as a catalyst (also included in complex catalysts) in various high-temperature chemical processes. The chemical nature of the Al_2O_3 surface is determined by the structural features of Al_2O_3 . Al_2O_3 containing metastable forms (γ -, η -, θ - Al_2O_3) is mainly used to prepare catalysts [49, 50]. The aluminum oxide we use in our spinel synthesis acts as an inert at low temperatures, preventing the product from melting. At the same time, it acts as a carrier of active sites on the surface. At high temperatures, aluminum oxide reacts with magnesium oxide to form spinel.

According to literature data, when molecules of an oxidizing agent, such as water, are adsorbed by a metal surface and bond through an oxygen atom, they exchange electrons. The oxygen atom donates at least a pair of electrons to the surface metal atoms. The outer part of the adsorbed molecule is positively charged and the inner part is negatively charged (double electric layer) [51]. Figure 10 shows a schematic of electron exchange during the chemical adsorption of water vapour molecules on the aluminum surface. Due to the high electronegativity of oxygen, the charge centers of the bonding electron pairs will be shifted towards the oxygen atom. As can be seen, when water vapor is adsorbed on the aluminum surface, the outer part of the adsorbed H_2O molecule is positively charged.

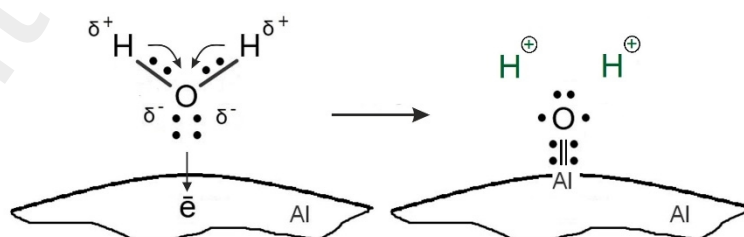
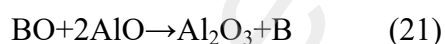


Fig. 10. Exchange of electrons during the chemical adsorption of water vapour molecules on the aluminum surface.

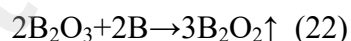
As the temperature rises, the vibration of charged particles increases. Hydrogen and protons are produced in the combustion wave during the oxidation of Al by water vapour.

Protons can also be produced from decomposition of boron hydrides contained in the initial boron. These compounds feature electron deficiency, the formation of bridging three-center two-electron B-H-B bonds, and clustering of boron atoms [25, 52].

The aluminothermic reaction of boron oxide with molten aluminum results in the reduction of boron. Aluminum oxidized to its oxide donates electrons to the boron and reduces it to the atomic state. After reaction (4), boron returns to the synthesis zone at high temperatures (800-1000 °C), when the initial boron has already burned out. The reduction of boron from the gaseous phase occurs at higher temperatures by the following reactions:



Evaporation of boron during combustion produces a thermally stable gaseous boron suboxide dimer B_2O_2 . It is formed at ~ 1000 °C by interaction of boron with molten B_2O_3 according to the reaction:



At high temperatures and pressures, a small amount of boron suboxide can also be formed, e.g:

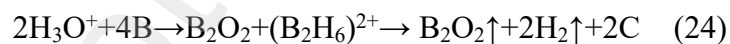


Gaseous boron compounds produced by combustion are reported in papers [24, 53-54]. Gaseous substances formed during synthesis in the boiling boron oxide melt can escape from the narrow channels of the product under high pressure, creating cavitation effects, which, in turn, can produce shock waves [55-58]. The calculated data presented in [59, 60] show a pressure exceeding 3000 atm at $t=0$ in the front of the shock wave created by cavitation effects.

A chain of parallel and consecutive exothermic reactions in the system causes a sharp increase in temperature. As a result of rapid SHS, aluminum and magnesium oxides in the starting

mixture become impregnated with melts of boron oxide and metallic aluminum, and saturated with gases (fluid) evolved during the reactions. Crystal formation in such a medium is accompanied by a sharp increase in the sample volume (ΔV) due to the oxidation of aluminum ($\Delta V=+27.5$ vol.%) and the synthesis of spinel ($\Delta V=+8.3$ vol.%). Rapid crystal growth causes high compressive pressure. Diffusion processes that occur during spinel crystallization in a sample result in the overgrowth of pores, the merging of small pores into larger ones, and partial recrystallization. Thus, the sample is a dynamically changing object. Atomic boron is also formed here. The small radius (Table 1) allows the boron atom to penetrate the interstitial space and occupy defects in the spinel lattice (vacancies, dislocations etc.). High synthesis temperature, rearrangement of crystal structures and rapidly growing spinel crystals create enormous pressure on the impurities and gases trapped in pores and between grains. In [61] showed how different pressure could affect in separate grains during compression.

High temperatures and pressures, the reduction of boron with aluminum, the formation of protons and hydronium ions on the aluminum oxide surface and their interaction create conditions for the proton-boron reaction.



Boron in a vapor-hydrogen mixture is known to form borohydrides [54]. If hydronium ions are involved in the oxidation of boron, then an unstable positively charged borohydride complex with a deficit of electrons can be formed. Figure 11 shows a schematic of boron oxidation by a hydronium ion with the formation of carbon. The circles indicate the number of electrons in the valence shell. Being a powerful electron acceptor, the proton can penetrate into the boron atom which is partially deprived of electrons. It (^1_1p) can capture an electron from the atomic shell, transforming into a neutron (^1_0n) with the simultaneous emission of neutrinos ν_e .

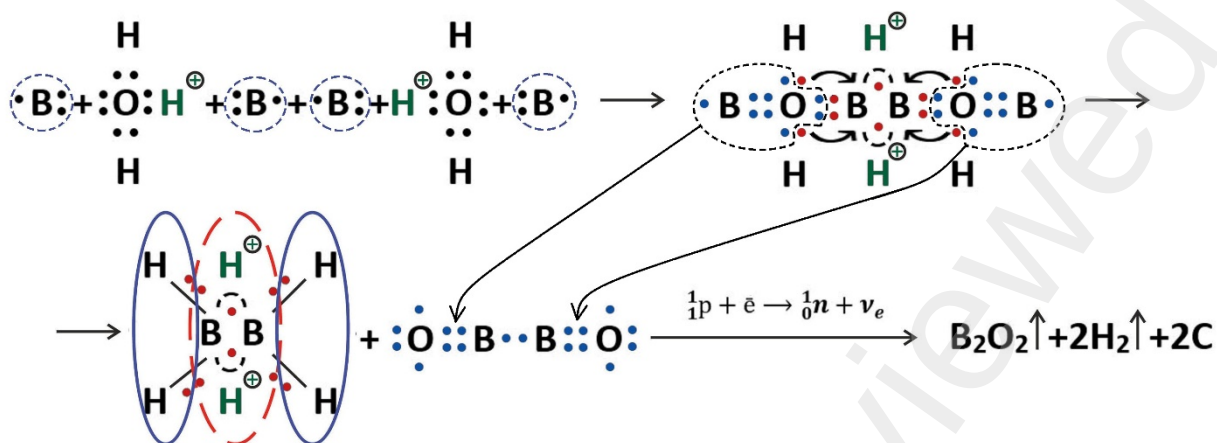


Fig. 11. Schematic of the oxidation of boron by a hydronium ion to form carbon.

In Eq. (25), aluminum suboxide AlO is involved in the reaction along with boron. Since aluminum has a higher affinity for oxygen than boron, aluminum reacts more readily with oxygen than boron.

The combustion gases were examined using an HR 4000CG-UV-NIR spectrometer (Ocean Optics, 200÷1100 nm wavelength range, 0.2 nm optical resolution). Combustion was monitored by video recording (MotionPro X3 camera, 10,000 fps, 10 μ m spatial resolution).

Emission spectra of combustion products during SHS of magnesium aluminate spinel with the addition of boron (2 wt.%) are shown in Fig. 12 as a function of the synthesis time. The temperature of escaping combustion gases was measured with a spectrometer. Hydrogen is evolved at 1620 °C (curve 1). The selective spectrum (curve 2) contains mainly molecular hydrogen bands. Low-intensity atomic emission lines of Al, O (with a different degree of ionization), and He are observed. The formation of helium confirms the LENR reaction. The spectrum with atomic helium (He I) lines at 355.44 nm and 452.98 nm is enlarged in the figure. Gaseous boron oxides are not detected except for BO₂.

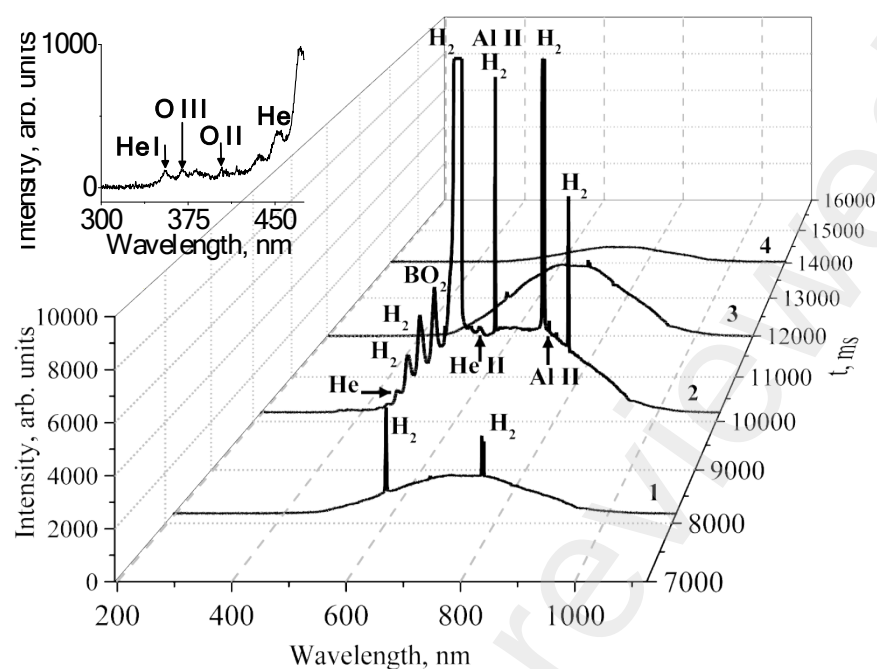


Fig. 12. Emission spectra of combustion products during SHS of magnesium aluminate spinel with the addition of boron as a function of the combustion time.

Ionized gases detected in the spectrum suggest the formation of low-temperature plasma in the combustion zones. Ionization is an endothermic process of the formation of ions from neutral atoms or molecules. Table 1 shows the ionization energies of an electron detached from a neutral atom for boron and aluminum. Charged particles (positive ions and electrons) formed in gases due to high temperatures and different radiations. In our case, we observed a bright glow during combustion, caused by the transition of excited electrons from higher energy levels to lower ones.

In Fig. 12 (curve 3), the observed increase in temperature up to 1790 °C occurs practically without gas release, which is associated with spinel crystallization from the gas phase. At the same time, boron reduction from aluminum and boron suboxides occur (Eqs. 20 and 21). The proton-boron reaction proceeds in local volumes. The studies showed that LENR reactions are local, i.e. occur in separate zones. In the anomalous sample, these reactions are more intense, apparently, due to the proton-boron reaction proceeding between ionized boron and hydrogen particles in a thermal explosion mode.

Thus, carbon is formed in the samples by two mechanisms. The first mechanism involves the interaction of hydronium ions with the boron reduced from the melt. A sharp increase in temperature during exothermic reactions and an increase in pressure due to rapid crystal growth in the melt saturated with gaseous reaction products in a dynamically changing system, trigger the proton-boron reaction with the formation of carbon. The second mechanism involves the LENR reaction by the proton-boron mechanism from ionized gases in low-temperature plasma.

Due to the chemical inertness of MgAl_2O_4 to carbon at high temperatures, the formed carbon is retained in the pores and intergranular space of spinel. The reducing conditions of synthesis, supported by significant hydrogen release, and the rapid cooling of the samples prevent carbon oxidation.

4. Conclusion

Microcrystals of carbon with a diamond-like lattice were synthesized through the proton-boron reaction during the SHS of magnesium aluminate spinel in the $\text{MgO-Al}_2\text{O}_3\text{-Mg(NO}_3)_2\cdot 6\text{H}_2\text{O-Al}$ system with the addition of 2 wt.% boron.

A possible mechanism of carbon formation was presented.

Water molecules separated from $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ crystalline hydrate and boric acid, contained as an impurity in amorphous boron, participate in the formation of hydrogen molecules, protons, and hydronium ions.

Protons are formed in three ways: at proton-transfer sites on the surface of aluminum oxide, by oxidation of water molecules on aluminum (boron), and by decomposition of borohydride compounds.

Rapidly growing spinel crystals lead to enormous pressure on impurities and gases in the intergranular space and in closed pores. Melt saturated with gaseous products creates additional pressure due to cavitation processes.

There are two mechanisms of carbon formation. The first mechanism involves the interaction of hydroxonium ion and boron in the melt saturated with evolved gases. Rapid compression produced by crystal growth, accompanied by cavitation processes occurring in the boiling boron oxide melt, leads to the formation of carbon through a proton-boron reaction. The second mechanism involves the formation of carbon in pores and defects of a crystal lattice from ionized gases of low-temperature plasma, triggering a proton-boron LENR reaction. The thermal explosion synthesis promotes the formation of the lonsdaleite phase with a diamond-like lattice.

Hydrogen released during spinel synthesis and rapid cooling of the sample prevent carbon oxidation. Helium fixed in the gases during combustion confirms the existence of a local LENR reaction. Intense combustion zones were observed in the anomalous sample. This seems to be associated with additional reactions in ionized gases in the thermal explosion mode. It is shown that the LENR reaction can occur at relatively low temperatures.

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