Synthesis of oxide and nitride ceramics in high-power gyrotron discharge

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Abstract. Synthesis of oxides, nitrides, and oxynitrides of silicon and aluminium by a pulsed microwave discharge in the mixtures of metal and dielectric powders is described. The microwave pulses were generated by high-power gyrotron (frequency 75 GHz, power up to 550 kW, pulse duration from 0.1 to 15 ms). \( \text{SiO}_2 + \beta\text{-Si}_3\text{N}_4 \) (1:1 by molar) and \( \alpha\text{-Al}_2\text{O}_3 + \text{AlN} \) (2:1 by molar) mixtures with Mg (1 and 5 wt%) were treated in air with microwave pulses with power of 250–400 kW and duration of 2–8 ms. It was found that the discharge cannot be initiated for both mixtures in absence of Mg at any pulse power and duration. When 1% of Mg was added, the discharge was observed for both mixtures under 8 ms pulses of 400 kW; however, the amounts of materials produced were not enough for analysis. With 5% of Mg the discharge was observed for both mixtures under 8 ms pulses of 350 kW, and products of the plasma-chemical processes in the \( \text{Al}_2\text{O}_3 + \text{AlN} \) mixture were analyzed.

1. Introduction
Ceramic materials are widely used in modern technology due to their unique mechanical and physical properties. Plasma methods are among the most promising techniques for the synthesis, modification, and processing of micro- and nanostructured ceramic materials[1–3]. There have been many examples of nanostructured material syntheses using various discharges: spark, arc, glow, high-frequency, microwave, and so on. Gyrotrons, being one of the most powerful sources of microwave discharges, are also used for the technologies mentioned, however, their application is rather limited to the experiments on high-density ceramics sintering [4] and deposition of thin films [5,6].
Recently we have shown that gyrotron discharge in mixtures of metal and dielectric powders can be used for synthesis of micro- and nanostructured materials. The synthetic approach was developed on a special stand incorporated into the standard design of the MIG-3 gyrotron complex [7]. The complex consists of two gyrotrons with a total power up to 1.5 MW. It was constructed in 2012 for plasma generation and heating in the L-2M stellarator. The plasma-chemical experiments were carried out in a specially constructed reactor [8] using gyrotron with a power up to 0.55 MW, frequency of 75 GHz, and microwave pulse duration between 0.1 and 15 ms. An actual gyrotron power was measured with a calorimeter [9]. The discharge was initiated in Ti + B, Mo + B, W + B, Mo + W + B, Mo + BN, Ti + KBF$_4$, and Mg + CB$_4$ mixtures in the air and nitrogen atmospheres [8,10,11]. It was found that the surface temperature of the powder mixture in the breakdown phase for these discharges was 2000 to 5000 K, while the temperature in the plasma–gas layer reached 10000 K [11]. The main products of the process were metal and boron oxides and metal borides [10,11]. Also formation of BN was found in some cases.

Here we describe our results of studies of plasma-chemical reactions under high-power gyrotron-initiated discharge in mixtures of metal and dielectric powders. We consider the possibility of obtaining new oxide, nitride and oxynitride materials from SiO$_2$ + β-Si$_3$N$_4$ and α-Al$_2$O$_3$ + AlN mixtures.

2. Experimental

The initial materials used were commercial powders of AlN (chemical grade, AlN powders for sealants), α-Al$_2$O$_3$ (chemical grade), SiO$_2$ (pyrogenic, Cabot), and Mg (chemical grade, Sigma-Aldrich). Initial powder of β-Si$_3$N$_4$ was prepared by self-propagating high-temperature synthesis at the Institute of Structural Macr0kinetics and Materials Science RAS (Chernogolovka) [12].

The materials produced in plasma were analyzed using X-ray diffraction analysis (Shimadzu XRD 6000 diffractometer, CuKα radiation, graphite monochromator, $\lambda = 1.54178$ Å) and energy-dispersive microanalysis using the EDMA, SEM JSM5910-LV with the analytical system INCA ENERGY. Scanning electron microscopy (JEOL JSM5910-LV, Zeiss Merlin) was used to get images of produced structures.

2.1. Synthesis in gyrotron-initiated discharge in metal-dielectric powder mixtures

Experiments were carried out with stand-mounted plasma-chemical complex of the MIG-3 installation described above. A specially designed plasma-chemical reactor (Figure 1, left) [8] was placed between two mirrors of the quasi-optical tract of the complex. Microwave breakdown in the reactor was initiated in air in the mixture of metal and dielectric powders placed on a quartz substrate with free upper surface (Figure 1, right). A quartz tube was set inside the reactor to collect the synthesized substances for further analysis. The gyrotron power was measured by a flow calorimeter. The evolution of direct and reflected gyrotron power during the microwave discharge was monitored using a system of microwave detectors, which were calibrated using the calorimeter [9].

The samples for plasma treatment (Figure 1, right) were prepared in the following way: 1-mm-thick layer of boron powder (2) followed by a 0.5-0.7 mm layer of metal-dielectric powder mixture (3) was put on the quartz plate (1). The layers were slightly squeezed with a flat quartz plate, and a quartz cylinder was installed over the plate. The plate with cylinder was set into the reactor. The upper surface of the powder remained open to ensure free plasma-gas-dynamic expansion of reaction products into the quartz cylinder volume.

The gyrotron microwave radiation was supplied through the bottom quartz plate. Irradiation of the samples was carried out with 5÷100 single 2÷12-ms pulses with intervals no less than 20 s. The gyrotron radiation power was 250÷400 kW which corresponds to intensity of ~6÷10 kW·cm$^{-2}$ inside the powder mixture. The Gaussian microwave beam with a characteristic radius of 40 mm penetrated the reactor volume and was absorbed in ceramic sinks located at a distance of 60 cm above the upper reactor exit window. The synthesized substances were deposited on both the walls of the quartz cylinder (6) and the remaining surfaces of the reactor including the upper quartz window.
Figure 1. Left: Plasma chemical reactor: 1 – hermetic chamber, 2 – exit quartz window, 3 – vacuum nozzle, 4 – diagnostic window. Right: General scheme of the reactor and measurements: 1 – quartz plate, 2 – boron powder layer, 3 – mixture of metal and dielectric powders, 4 – plasma, 5 – working gas, 6 – quartz cylinder (d = 70 mm, L = 350 mm). The arrows on the left-hand side indicate directions along which the microwave radiation was received by two cameras (#1, 2) and three spectrometers (#1, 2, 3).

2.2. Discharge parameters and evolution
The microwave glow discharge, powder and synthetic substances were observed through the viewing window in the plasma-chemical reactor. The evolution of integrated microwave glow discharge and afterglow phase was recorded by a high-speed camera «Fastec Imaging IN250M512» (camera 1 in Figure 1b) synchronized with measurements of three spectrometers. Figure 1b shows the locations of the three spectrometers. The time evolution of discharge radiation in the optical wavelength range was recorded with the help of three spectrometers «Ava-Spec» in the range 370 ÷ 920 nm with a resolution of 0.7 and 0.3 nm and in the range of 250 ÷ 800 nm with a resolution of 0.8 nm. From the recorded spectra we analysed evolution of characteristic atomic and molecular wavelengths of reaction components in the different sites of the reactor. The receiving system of spectrometer no. 1 was directed on the powder and allowed to record the glow of the powder surface as well as that of the plasma and gas phase (layers 2–4 in Figure 1b). The receiving systems of spectrometers no. 2, 3 were directed parallel to the powder mixture surface allowing to record radiation mainly from the plasma and gas regions of the discharge (layers 3, 4 in Figure 1b). In some experiments, one of the spectrometers was used to record radiation from the lower surface of the powder mixture. During a single microwave discharge, spectrometers recorded up to 100 optical spectra at intervals of about 4 ms.

3. Result and discussion
Previously it was shown that in order to transform the initial mixture of powders into a new material the gyrotron discharge parameters should be chosen so that the microwave discharge was followed by an afterglow phase [11]. Only under this condition almost complete absorption of microwave radiation of gyrotron in the powder mixture and initiation of chemical reactions of synthesis of substances was possible [13]. So we have treated the systems listed in table 1 with 2÷8 ms microwave pulses generated by gyrotron at power levels from 250 to 400 kW. For all the systems, no discharge was observed if the pulse duration was below 2÷6 ms at any power level. When the mixtures were treated with 8 ms pulses, the discharges were observed at the power level 400 kW both with Al- and Si-containing mixtures with 1% of Mg. However, it was not possible to collect significant amounts of the products (table 1, entries 3 and 4). When 5% of Mg was added to the mixtures, the discharges could be initiated at 400 kW power level (table 1, entries 5 and 6); but only in the case of Al-containing mixture we collected an amount of new product materials appropriate for analysis with SEM and XRD. Only
one pulse lead to the discharge for the systems with 1% of Mg, while up to three pulses were successful when 5% of Mg was added. This means that Mg is consumed during the discharge taking part in plasma-chemical processes.

**Table 1.** Results of microwave discharge initiation in the AlN + Al₂O₃ and Si₃N₄ + SiO₂ systems with 8 ms pulses of 250÷400 kW.

| Entry | System | 250 kW | 300 kW | 350 kW | 400 kW |
|-------|--------|--------|--------|--------|--------|
| 1     | SiO₂ + Si₃N₄ | no/no* | no/no  | no/no  | no/no  |
| 2     | Al₂O₃ + AlN | no/no  | no/no  | no/no  | no/no  |
| 3     | SiO₂ + Si₃N₄ + 1% Mg | no/no  | no/no  | no/no  | yes/no |
| 4     | Al₂O₃ + AlN + 1% Mg | no/no  | no/no  | no/no  | yes/no |
| 5     | SiO₂ + Si₃N₄ + 5% Mg | no/no  | no/no  | yes/no | –      |
| 6     | Al₂O₃ + AlN + 5% Mg | no/no  | no/no  | yes/yes| –      |

*Discharge initiated/significant amount of products formed in plasma-chemical process.

SEM images of the obtained materials are given in Figure 2 (top and bottom left). One can see that the material basically consists of amorphous particles 2-10 microns in size and well-shaped spherical crystals. Elemental analyses showed that spherical crystals mostly consist of Mg, Al, and O, so one can assume that the crystals are MgAl₂O₄. XRD-analysis confirmed the suggestion (Figure 2, bottom right). Characteristic diffraction peaks of MgAl₂O₄ spinel were identified in XRD pattern, although according to XRD data MgAl₂O₄ is not a major phase, which is actually aluminum nitride AlN coming most likely from starting material. Thus, we can conclude that plasma-chemical processes under microwave discharge in the mixtures of metal and dielectric powders can lead to formation of new materials. These materials can be highly dispersive and show high crystallinity.

**Figure 2.** Top: SEM-images of products from the system 6. Bottom left: Element mapping of products from the system 6. Bottom right: XRD pattern of products from the system 6.
4. Conclusions

Usability of the microwave discharge generated by high-power gyrotron in mixtures of metal and dielectric powders for synthesis of oxide and nitride ceramic materials containing Al and Si was demonstrated. It was shown that the discharge cannot be initiated in mixtures of dielectric powders Al₂O₃ + AlN and SiO₂ + Si₃N₄ even with 8 ms pulses of 450 kW. Addition of 1wt% of Mg allowed, in principle, to initiate the discharge with 8 ms pulses of 400 kW, and 5% is enough for obtaining significant amounts of new synthesized materials including micro dispersed magnesium aluminate MgAl₂O₄. SEM images showed that microcrystals of MgAl₂O₄ are well shaped. XRD analysis confirmed spinel structure for them.

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