Plasma-chemical processes in the mixtures “metal-organic compound” and “metal-inorganic salt” initiated by pulse radiation of gyrotron

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Abstract. Plasma-chemical processes in the mixtures of metal+organic compound and metal+inorganic salt under treatment by microwave pulses are 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). Al + melamine (1:1, 2:1 and 3:1 by molar) and Al + Al2O3 + NH4Cl (1:2:2 and 1:2:4 by molar) were treated in air with microwave pulses with power of 150–350 kW and duration of 2–8 ms. It was found that the discharge can be easily initiated for both mixtures at minimal pulse duration of 2 ms. For Al + melamine mixture the energy threshold for the discharge depends linearly on the mass content of Al and does not exceed 1.0 kJ/g. For Al + Al2O3 + NH4Cl the threshold is also below 1.0 kJ/g. The products of treatment of Al + melamine contain mainly starting materials and no nitride phases, in case of Al + Al2O3 + NH4Cl some traces of Al11O15N were identified.

1. Introduction
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].

Several years ago we started our investigations of the effects in the mixtures of metal and dielectric powders induced by microwave pulses. It was found that the pulses generated by high power gyrotron (pulse duration 0.1–15 ms, pulse power 0.55 kW, 75 GHz) initiate the discharges and formation of low temperature plasma. The experiments were carried out using specially designed reactor [8]. An actual gyrotron power was measured with a calorimeter [9]. In the very first experiments the discharge was
successfully initiated in the mixtures Ti + B, Mo + B, W + B, Mo + W + B, Mo + BN, Ti + KBF$_4$ and Mg + CB$_4$ mixtures under the air and nitrogen [8,10,11]. The surface temperature of the powder mixture in the breakdown phase was determined to be from 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, metal borides and BN in some cases [10,11].

Recently we have focused on Al + Al$_2$O$_3$, Al + AlN, Al + Al$_2$O$_3$ + AlN and some other closely related mixtures in order to prepare the particles of aluminum oxynitride phases (AION). Aluminum oxynitride is a ceramic material with high physical, mechanical and optical properties, which is widely used in different areas of technology, however, its preparation is still a challenge since it requires high temperature and pressure [12]. Using different additives, e.g. melamine as a source of nitrogen and carborane C$_2$B$_{10}$H$_{12}$ as a source of hydrogen (which is necessary for reductive nitridation process), we succeed in obtaining the particles of aluminum oxide with nitridated surface containing aluminum oxynitride phases Al$_{11}$O$_{15}$N and Al$_{27}$O$_{39}$N [13].

Herein we continue our study Al-based systems and present the results for mixtures Al + melamine and Al + Al$_2$O$_3$ + NH$_4$Cl (under the air). It was found that the microwave discharge can be easily initiated for the mixtures metal + organic compound and metal + inorganic salt (+Al$_2$O$_3$). We couldn’t identify any nitride phases in case of Al + melamine mixtures, which strongly supports our hypothesis that oxynitrides in the systems Al + Al$_2$O$_3$ + melamine form via nitridation of oxide and not via oxidation of nitrides. In case of Al + Al$_2$O$_3$ + NH$_4$Cl some traces of Al$_{11}$O$_{15}$N phase were found in the products.

2. Experimental

The initial materials used were commercial powders of Al (PAP-4, technical grade), α-Al$_2$O$_3$ (chemical grade) and melamine (chemical grade, Sigma-Aldrich).

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.

The experiments were carried out on the MIG-3 plasmochemical complex. The MIG-3 setup is an electron-cyclotron plasma heating system for the L-2M stellarator with a gyrotron 75 / 0.8 (operating frequency 75 GHz, pulse duration up to 12 ms, power up to 550 kW) [2].

Figure 1. Left: the layout of the plasma-chemical reactor (C) in the quasi-optical path (B) of the gyrotron (A); right: flow chart of the process and data collection in the plasma-chemical reactor (C).
The gyrotron pulse (A) is sent through a system of copper mirrors forming a quasi-optical path (B) to a specially developed plasma-chemical reactor (C) [3] (fig. 1). Measurement of the actual power of the gyrotron is carried out by a flow calorimeter. The parameters of transmitted and reflected microwave beams are measured by a system of microwave detectors, which are also calibrated using a flow calorimeter. Sample (3) is placed on a quartz substrate (1), forming a layer ~1 mm thick. Also an isolating layer of dielectric powder (2) can be placed between substrate (1) and sample (3) if needed. The sample layer (3) is slightly compacted with quartz glass. When a microwave pulse passes through the sample, a discharge occurs, as a result of which a significant part of the particles rises above the surface of the sample, plasma (4) and the gas phase (5) are formed. The development of plasma-chemical processes is visually controlled through the quartz windows (6) and (7) using a high-speed Fastec Imaging IN250M512 camera (8) and a regular camera (9), as well as three Ava-Spec optical spectrometers (10–12) operating in the range of 250–920 nm. In a standard experiment, spectrometers record 100 spectra with an interval of 4 ms after the passage of a microwave pulse. To collect the products of the process, a quartz cylinder (13) is installed in the reactor. All the experiments were carried out under nitrogen atmosphere, preset pressure in the reactor was 1 bar.

3. Result and discussion
First we studied Al + melamine mixtures with a component ratio of 1 : 1, 2 : 1 and 3 : 1 (by molar). For all the listed mixtures the discharge can be easily initiated at minimum pulse duration (2 ms). The pulse power needed for breakdown decrease with increase of aluminium content. It was found that the energy threshold for initiation of the discharge does not exceed 1 kJ/g and show linear dependence on the mass content of aluminum in the mixture (Fig. 2). In principle, the energy threshold is expected to depend on the metal surface and as far as the metal powder is the same in all the mixtures, so the particles size is also the same and the surface increase in the same order as the mass content of metal.

| Al : melamine | Pulse power, kW | Pulse duration, ms | Energy threshold, kJ/g |
|---------------|-----------------|-------------------|------------------------|
| 1 : 1         | 350             | 2                 | 0.7                    |
| 2 : 1         | 250             | 2                 | 0.5                    |
| 3 : 1         | 150             | 2                 | 0.3                    |

Figure 2. Parameters of pulses initiating a discharge in Al + melamine mixtures (left) and the dependence of the energy threshold on mass content of aluminum (right).

The main feature of the optical spectra recorded by spectrometer 10 above the surface of the powder is a presence of separate molecular bands observed above the continuum. Particularly, in the range of 492–516 nm the band of C_2 molecule was fixed and this band was used to determine the temperature in zone (5) (Fig. 3). According to the obtained data the gas temperature reaches 3500 K. An X-ray phase analysis of the substance deposited on the walls of the quartz cylinder 13 showed that it consists of aluminum metal and melamine (Fig. 3), i.e. source components. Also some traces of α-Al_2O_3 were identified, however, no potential products interaction of Al and Al_2O_3 with melamine (i.e. nitride and / or carbide phases of aluminum) was found. For sure, melamine is not able to withstand the temperature ~3500 K, however, such a high temperature is kept for a very short time only, so one can assume that the large particles do not have enough time to decompose completely and the residues are found as a part of products.
Earlier we proposed that oxynitride phases form in $\text{Al} + \text{Al}_2\text{O}_3 + \text{melamine}$ mixtures as a result of nitridation of $\text{Al}_2\text{O}_3$ and not as a result of consequent nitridation of aluminum and oxidation of aluminum nitride. The results for $\text{Al} + \text{melamine}$ mixture strongly support that proposal.

Fig. 3. Left: the optical spectrum recorded by spectrometer 10 for an experiment with a mixture of $\text{Al} : \text{melamine} = 3 : 1$ 4 ms after the passage of the pulse; right: diffractogram of a substance deposited on the walls of a quartz cylinder 13.

For $\text{Al} + \text{Al}_2\text{O}_3 + \text{NH}_4\text{Cl}$ mixtures with component ratios of $1 : 2 : 2$ and $1 : 2 : 4$ the discharge is also initiated by pulses of 2 ms duration and power up to 350 kW, and the energy thresholds again do not exceed 1 kJ / g. An X-ray phase analysis of the substances deposited on the walls of the quartz cylinder (13) showed trace amounts of oxynitride phases, one of them was identified as $\text{Al}_{11}\text{O}_{15}\text{N}$. Earlier the same phase was found in the products after treatment of the mixtures $\text{Al} + \text{Al}_2\text{O}_3 + \text{melamine}$ [13]. So we can see that in contrast to metal aluminum the $\text{Al}_2\text{O}_3$ undergoes nitridation by melamine and its presence is really needed for formation of aluminum oxynitrides.

4. Conclusion
The obtained data once again show the advantages for using of microwave discharge initiated by the pulses of high power gyrotron in the powders mixtures metal + dielectric to synthesize new materials. Some proposals about the basic principles of mechanism for formation of aluminum oxynitrides were confirmed. Also we demonstrated the possibility of using of organic substances and inorganic salts as components of the mixtures (not only as additives). Moreover, they were found to decrease the threshold for discharge initiation (less than 1 kJ/g vs. 1.5±2.5 kJ/g).

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