Synthesis of new materials through microwave discharge initiated by pulses of high power gyrotron in the mixtures of metal and dielectric powders

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Abstract. Herein we describe a new plasma chemical method for synthesis of new materials. Plasma was generated as a result of microwave discharge initiated by pulses of high power gyrotron in the mixtures of metal and dielectric powders. The gyrotron operates at frequency of 75 GHz giving pulses with duration of 2-12 ms and power up to 550 kW. Mixtures of Al with Al2O3, AlN, melamine and NH4Cl were treated with the pulses in the specially constructed plasma chemical reactor, which allowed to collect products of the process and to carry out real time monitoring of the process with low- and high-speed cameras and spectrometers. We observed a complicate oscillating process, which led to formation of micro dispersed materials containing phases usually formed at high temperatures. It was shown that plasma temperature in all the experiments was at least 2500 K in all reaction areas and above 3500 K in main reaction zone. We also realized that addition of hydrogen-containing substances (e.g. C2B10H12) resulted in a noticeable intensification of the process – highly likely due to the change of reactions pathways through an involvement of hydrogen into the intermediate stages. Obtained data confirm that microwave discharge is a promising method for synthesis of new materials including fine structure materials, e.g. consisting of major phase micro particles covered with a thin layer of minor phase.

1. Introduction
Plasma-chemical processes play an essential role in modern materials science. They are widely used for the synthesis and subsequent processing of various materials. Non-equilibrium conditions of the processes allow obtaining phases of a unique composition. That also makes possible the formation of thin films on different substrates. Plasma can be generated by several methods and is classified as ideal and non-ideal, low-temperature and high-temperature, equilibrium and non-equilibrium. A low-temperature plasma with a temperature below 10^4 K is mainly used for the synthesis of materials. Particularly, this type of plasma can be generated by treatment of mixtures of metal and dielectric...
powders with pulses of high-power microwave irradiation. If microwave irradiation is absorbed effectively than energy can release as a powerful discharge, which leads to columbic explosion and heating of mixture up to 10^4 K.

Earlier we have shown that the discharge can be initiated in mixtures of Ti + B, Mo + B, W + B, Mo + W + B, Mo + BN, Ti + KBF_4 and Mg + CB_4 in air and nitrogen [1-3]. The temperature of the powder surface at the initial stage of the process ranges from 2000 to 5000 K, while the gas phase temperature rises up to 10000 K [3]. New materials form through the plasma-chemical process and include metal oxides and borides, boron oxide and in some cases boron nitride. Herein we describe our latest results obtained for mixtures of Al with Al_2O_3, AlN, melamine and NH_4Cl, which have been studied for possible formation of aluminum oxynitrides — ceramic phases with high mechanical properties and thermal and chemical stability, which are used in different areas of material science and technology [4-7].

2. Experimental

2.1. Raw materials

The starting materials used were powders of metal aluminum (technical grade, 98\%+, average size of particles ca. 4 \(\mu\)m), \(\alpha\)-Al_2O_3 (chemical grade, average size of particles ca. 50 \(\mu\)m), and commercial AlN powder for sealants with the following composition: N \(\geq\) 33.0 wt\%, O \(\leq\) 1.2\%, Fe \(\leq\) 0.1\%, and C \(\leq\) 0.05\%; purity is 96\%+ (average size of particles ca. 20 \(\mu\)m). Al(NO_3)_3\(\cdot\)9H_2O, NH_4Cl, C_2B_10H_12 and melamine C_3H_6N_6 of chemical grade were used as supplied.

2.2. General experimental procedure

The experiments were carried out with the plasma-chemical complex MIG-3 (Figure 1). The MIG-3 installation 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]. The gyrotron pulse (1) is directed to a specially designed plasma-chemical reactor (3) [3] through the system of copper mirrors forming the quasi-optical path (2). Measurement of the actual power is carried out with a flow calorimeter. The parameters of the transmitted and reflected microwave beams are measured with a system of microwave detectors, which are also calibrated with a flow calorimeter. Sample (4) is placed on a quartz bottom (5) forming a layer of ca. 1 mm thick. The layer is slightly condensed with quartz glass. When microwave radiation pulse passes through the sample (4) a discharge occurred. As a result, a significant part of the particles rise above the sample surface and plasma (6) and gas phase (7) are formed. The development of plasma-chemical processes is monitored visually using a high-speed camera Fastec Imaging IN250M512 (8) and 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 pulse. A quartz cylinder (13) is installed in the reactor to collect the process products. The reactor can be filled with air or any gas.

3. Product characterization

Particles size distributions were measured with Fritsch Laser Particle Sizer Analysette 22 which utilizes laser light scattering method. The measurements were carried out for wet dispersions prepared using water as a solvent. The phase composition was determined by X-ray diffraction analysis (Shimadzu XRD 6000 diffractometer, Cu \(K_\alpha\)-radiation, graphite monochromator, \(\lambda = 1.54178\) \(\text{\AA}\)). ICDD database was used to identify the phases. SEM-images of the samples were taken with using VEGA II TESCAN microscope at 20 kV acceleration voltage.
4. Results and discussion

4.1. Key stages of plasma chemical process

As it was mentioned before, microwave discharge can be successfully initiated in the mixtures of metal powders and powders of ceramics, which are classical dielectrics. We studied the discharge and following plasma chemical processes in mixtures of Al with Al₂O₃ and AlN and then proceeded with salts (Al(NO₃)₃·9H₂O, NH₄Cl) and organic substances (melamine C₃H₆N₆). Also, we checked an effect of addition of carborane C₂B₁₀H₁₂ as a kind of catalyst, since it has been shown recently that hydrogen-rich compounds (C₂B₁₀H₁₂ or H₃BO₃) prolonged the main stage of the process (see below). All the studied mixtures are listed in Table 1.

Table 1. Mixtures and conditions of experiments.

| No | Mixture (molar ratio) | Gas | Threshold energy, kJ/g | Phase composition |
|----|----------------------|-----|------------------------|------------------|
| 1  | Al/Al₂O₃ (1:2)       | nitrogen | 1.1-1.7 | Al, α-Al₂O₃         |
| 2  | Al/AlN (4:1)         | air   | 0.5-0.6 | Al, α-Al₂O₃, AlN    |
| 3  | Al/Al₂O₃/AlN (2:1:1) | air   | 0.7-1.4 | Al, α-Al₂O₃, AlN    |
| 4  | Al/Al(NO₃)₃·9H₂O (14:1) | nitrogen | 0.7-0.8 | Al, α-Al₂O₃         |
| 5  | Al/Al₂O₃/melamine (1:2:1) | nitrogen | 1.1-1.7 | Al, α-Al₂O₃, Al₁₁O₁₅N, Al₂₇O₃₉N |
| 6  | Al/Al₂O₃/melamine (1:2:1)+5 w/w% C₂B₁₀H₁₂ | nitrogen | 1.1-1.7 | Al, α-Al₂O₃, Al₁₁O₁₅N, Al₂₇O₃₉N |
| 7  | Al/melamine (1:1)    | nitrogen | 0.7 | Al, melamine        |
| 8  | Al/melamine (2:1)    | nitrogen | 0.5 | Al, melamine        |
| 9  | Al/melamine (3:1)    | nitrogen | 0.3 | Al, melamine        |
| 10 | Al/Al₂O₃/NH₄Cl (1:2:2) | nitrogen | 0.6-0.7 | Al, α-Al₂O₃, NH₄Cl  |
| 11 | Al/Al₂O₃/NH₄Cl (1:2:4) | nitrogen | 0.6-0.7 | Al, α-Al₂O₃, NH₄Cl, Al₁₁O₁₅N |

We have realized that the discharge can be initiated in all the studied mixtures. All the mixtures effectively absorb energy of microwave irradiation and absorption coefficients vary from 90 to 98% being mainly in the range from 95 to 98%. Threshold energies vary widely and strongly depend on the content of metal in the mixture as it could be expected. Considering a series of Al/melamine mixtures we concluded that threshold energy depends linearly on the volume content of Al.

If the discharge is initiated, it leads to coulomb explosion in the mixture. As a result a significant amount of particles rise up into the volume of the reactor, the temperature increases quickly and
dramatically, so several processes occur at the same time including melting of particles, evaporation of substance into the gas phase, dissociation of molecules in the gas phase and reactions in the gas phase and on the surface of solid and melted particles. At this moment a bright flash can be observed, this is the first stage of general plasma chemical process — initiation stage.

After that two pathways for the process are possible. The first one is a rapid fading of the process as soon as the system cools down due to heat dissipation. However, if the reactions proceed fast enough and generate required heat amount then they can switch into autothermic oscillating mode and the process can last for reasonably long time. That was exactly what we observed for all the studied mixtures. From high-speed camera it can be seen clearly, that glowing of particles oscillate and the same picture we got from optical emission spectroscopy. We estimated plasma temperature in the beginning basing on Wien’s displacement law from optical spectra recorded by spectrometer (12). According to the obtained results the temperature in the bottom of reactive zone is ca. 2500±250 K. Temperature on the top of reactive zone cannot be determined directly from spectrometer (11) data due to quick clouding of top reactor’s window, but we are quite confident that temperature in this area is above 3500 K, because AlO spectrum was observed and AlO forms in gas phase at 3533 K.

The oscillations continue for 40-160 ms which is 1-2 orders longer comparing to pulse duration (2-6 ms). The maximum time is achieved if C2B10H12 is added as a source of hydrogen (see entry 6 in Table 1). The specific role of hydrogen in plasma chemical processes has been shown recently, for example, for preparation of BN nanotubes in the presence of H2 [8]. We showed that hydrogen-rich substances can be used instead of gaseous hydrogen which has an evident advantage from the safety point of view.

The final stage is a quick fading of the process followed by condensation of substances from the gas phase on the surface of particles and deposition of particles on the walls of quartz well (13). Then the products of the process can be collected and analyzed.

4.2. Products characterization

The products of plasma chemical processes were analyzed in terms of particles size distributions (laser light scattering), morphology (SEM) and phase composition (XRD). Considering particles size distributions, it should be noted that share of small size particles (< 20 μm) is much lower in products against starting mixtures. This is contrary to what we could expect considering only gravity influence, so we believe it to be a clear sign that the matter is redistributed between the particles during the process through melting, evaporation and condensation.

Morphology of the particles confirms that suggestion (Figure 2). As one can see there are a lot of particles of spherical shape with rounded or just slightly faceted surface, i.e. edges are melted, and all the particles are less of the same size of 40-60 μm.

Phase composition according XRD data is also given in Table 1. When the process occurs in the air aluminum oxide always forms as well as in the case of Al/Al(NO3)3·9H2O. No traces of nitride or oxynitride were found which means that oxidation prevails over nitridation. Moreover, direct nitridation of aluminum didn’t occur even under nitrogen atmosphere in Al/melamine (C3H6N6) mixtures. However, if the mixture contained aluminum oxide and melamine and was treated under nitrogen, then small amount of oxynitride phases (Al11O15N, Al27O39N) formed. Al11O15N formation was also observed for the mixture of Al, Al2O3 and NH4Cl, which was treated under nitrogen atmosphere. So, we can conclude that oxynitride phases formed through nitridation of aluminum oxide. Considering a low content of nitrogen in these phases one can assume that nitridation proceeded on the surface of aluminum oxide particles. Thus, the particles highly likely have a core-shell structure with an aluminum oxide core and thin aluminum oxynitride shell.
5. Conclusions
We studied plasma chemical process under microwave discharge initiated by pulses of high power gyrotron in the mixtures of metal and dielectric powders. It was shown that the process can be divided into three main stages. The first initiation stage follows the discharge and consist in melting and evaporation of starting materials and dissociation of molecules in the gas phase, energy threshold for initiation varies from 0.5 to 2.0 kJ/g and depends mainly on the volume concentration of metal in the treated mixture. The main stage is an oscillating process, which is up to several orders longer comparing to pulse duration and includes different reactions in gas phase and on the surface of solid particles and drops of melted materials. The final stage is condensation of formed substance from gas phase and crystallization with following deposition of the particles on the walls of the reactor. It was shown that the time of main stage can be sufficiently prolonged if the mixture contains a source of hydrogen, which is most likely due to high exothermic effects of possible hydrogen reactions. We also showed that nitrogen-containing compounds can promote nitridation reactions, which lead to formation of oxynitride phases in case of Al/Al₂O₃ mixture. The oxynitrides formed on the surface of Al₂O₃ particles, so the developed method is applicable for synthesis of materials with core-shell particles structure.

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