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PREPARATION OF NANOSTRUCTURED ENERGETIC MATERIALS BY SOL-GEL TECHNOLOGY

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The conditions have been experimentally specified for formation of a xerogel of nano-structured energetic materials by the sol-gel method. Using an example of the system of resorcinol-formaldehyde and ammonium perchlorate, the limiting factors for the formation of nano-particles were found to include: the water content in the primary sol, the solubility of ammonium perchlorate, and the rate of drying of the gel formed. It has been found that increased temperature results in distinct shortening of the time of formation of the gel.

Introduction

Research and development in the area of substances and materials of sub-micron dimensions is one of intensely monitored and constantly developing fields. In the

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past decades it has been shown that particles of nanometer dimensions possess a number of specific properties, which can be utilised in microelectronics, biochemistry, medicine, optoelectronics, adhesion techniques, composite materials etc. [1].

This trend can also be observed in the area of energetic materials (EM). The interest in nano-structured energetic materials (NEM) is motivated by the efforts directed to achieving of high energy content per volume unit, which can be released during explosion transformation. In principle, this aim can be reached in two ways: (i) synthesis of an individual explosive with high density, or (ii) preparation of an oxidant-fuel mixture, again with high density.

In a rapid explosion transformation (detonation), the molecule of individual explosive is first decomposed to particles (atoms or groups of atoms) that subsequently react to give stable products of lower inner energy. Since the transformation takes place at high pressures (tens of GPa) in the original volume of the molecule, the rate of the process is determined kinetically.

In oxidant-fuel mixtures the first process is decomposition of the two components; they must subsequently get within a reaction distance and react with each other. The time of active collision is distinctly prolonged, and the rate of the process is determined by mass transfer. As the average magnitude of a molecule of explosive is 1 nm, every effort is made to bring the two components as close to each other as possible, i.e. in the nm dimensions, and to reach high density and homogeneity of the oxidant-fuel mixture.

In principle, the preparation of NEM can be realised in two ways: either the nano-particles of oxidant and fuel are prepared separately (in chemical or physical way) and then mixed [2] or the preparation of nano-particles of both components and the resulting composite are performed simultaneously [3]. So far the greatest attention has been given to preparation of aluminium in nanometer particles (nAl), particularly the type ALEX [4], and other metals, using the first one of the above-mentioned variants. In similar way, nano-structured metal oxides were prepared, and their application was mainly directed to the mixtures of the thermite type [5]. The equipment needed for production of nano-particles is considerably costly and has been technologically realised only in few countries (Russia, USA).

At the conditions available to us, the second variant is considerably more appropriate, particularly the sol-gel method [6]. Its principle is preparation of homogeneous solution of fuel and oxidant in water (sol) and subsequent cross-linking that produces a three-dimensional polymeric network (gel). The pores of this gel contain a solution of oxidant, the oxidant being precipitated (in nm dimensions) by an exchange of solvent. The precipitating solvent must be infinitely miscible with water and must not dissolve the oxidant. The next operation is drying of the gel, which produces two types of product depending on the rate of evaporation: at low rate the product formed is dense and hard (the so-called xerogel); at high rate of evaporation (e.g. by super-critical extraction) the

product is highly porous (the so-called aerogel).

With regard to our interest in getting the highest possible volume energy, we focused our attention on the xerogel type. The original paper [6] describes the preparation of a three-dimensional polymeric system of resorcinol-formaldehyde (RF) as the fuel component containing encapsulated ammonium perchlorate (AP) as the oxidising component. As the procedure of preparation was only described in general, the same being true of the resulting xerogel, it was necessary to find out both the detailed conditions of preparation and the properties of the product.

Experimental

The chemicals used: resorcinol (min. content 98 %), ammonium perchlorate (min. content 99.5 %), sodium carbonate (min. content 98 %), formaldehyde (aqueous solution. 37 %), and distilled water. The properties of the final products were determined by means of the following apparatus: DTA 551-Ex, fallhammer BAM, and electron microscope JEOL JSM-5500LV.

Basic Procedure of Preparation of Polymeric Matrix Resorcinol-Formaldehyde (RF)

A solution was prepared by dissolving 2.4 g resorcinol, 3.4 g formaldehyde (37 %) and 0.025 g sodium carbonate in 40 g water at a temperature of 20 °C. The temperature was increased to 40 °C, and after 40 hours, an elastic brown gel resulted, which contained 70 % water. Drying (48 hours at room temperature) gave a hard and fragile gel.

Basic Procedure of Preparation of Xerogel RF-AP

A solution was prepared by dissolving 2.4 g resorcinol, 3.4 g formaldehyde (37 %), 2.2 g ammonium perchlorate, and 0.025 g sodium carbonate in 80 g water at a temperature of 20 °C. The temperature was increased to 40 °C, and after 46 hours, a transparent elastic brown gel was formed. It was fragmented to smaller pieces and digested twice with methanol and then dried at room temperature 2 days. The xerogel obtained was transparent, hard and fragile.

The measured densities were 1.33 g cm^{-3} for dry RF gel, and 1.45 g cm^{-3} for RF-AP xerogel. The calculated theoretical maximum density (TMD) for the mixture of RF and NH_4ClO_4 at a ratio of 64:36 is 1.50 g cm^{-3}. Hence the density of xerogel is higher than 95 % TMD.

The dimensions of AP particles were measured by means of a scanning electron microscope (SEM) (Fig. 1): it varies within the limits of 50 – 500 nm. The DTA record of the samples revealed a rapid intensive decomposition at 273 °C (Fig. 2). The impact sensitivity was $h = 50$ cm (hammer mass 5 kg).

Discussion

The described preparation of xerogel must respect several factors. One of them is the amount of water used for the formation of primary solution (sol). Long-term heating in an open system causes evaporation of water and simultaneous cross-linking of the RF matrix with formation of gel; the gel includes AP solution. The amount of this solution encapsulated in the gel structure has a limited volume (70 – 90 % of total volume of gel), hence the limiting factor for the oxidant (AP) is its solubility. With higher content of AP, the gel network is formed too, but it is accompanied by distinct efflorescence with large crystals. The exchange of solvent (water) by methanol causes formation of AP crystals (AP is almost insoluble in methanol) whose growth is limited by the gel matrix. The resulting crystals have the dimensions in nanometers.

The subsequent drying removes the solvent mixture present, and a solid xerogel is formed. Its physical condition is strongly affected by the rate of drying. At high rate of drying (a stream of air; vacuum), rapid diffusion of solvents takes place with concomitant formation of AP efflorescence and cracks in the xerogel even resulting in its fragmentation. Another consequence of the removal of solvents is the decrease in the original volume by up to tens of per cent. The resulting xerogel is hard and fragile, and its density is high. Although the oxygen balance is considerably negative, the DTA records reveal a strongly exothermic reaction. Similarly, the impact sensitivity test confirms the formation of nano-structured xerogel and, at the same time, its lowered sensitivity.

The SEM picture shows that the magnitude of particles varies within the limits of tens to hundreds of nanometers, i.e. within a rather broad scale. Nevertheless, it must be taken into account that at least one dimension does not exceed tens of nm, which results in sufficiently intimate contact between both components of the system.

The above-given basic procedure was varied in a number of experiments (the amount of water, the temperature of cross-linking and conditions of drying of

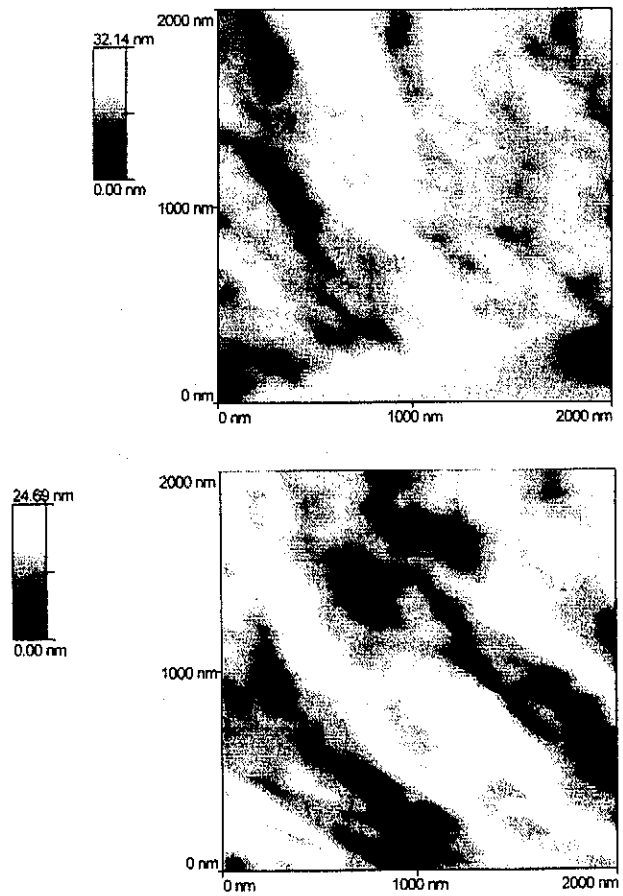

Fig. 1 SEM image of the xerogel RF-AP

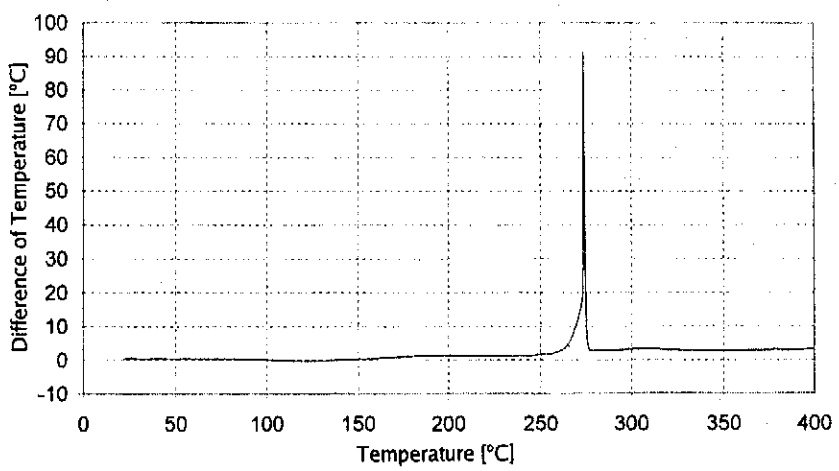

Fig. 2 DTA of the xerogel RF-AP

the gel formed). It was found that by increasing the temperature it is possible to distinctly shorten the time of preparation of gel without affecting the properties of the final product.

Conclusion

The limiting factors in the preparation of xerogel of required composition, based on resorcinol, formaldehyde and ammonium perchlorate, involve the amount of water in the primary sol, solubility of ammonium perchlorate in water, and rate of drying of the gel. Also the temperature distinctly affects the rate of formation of the gel. In the case of the system investigated it is possible to attain a density of dry xerogel that is higher than 95 % TMD, the magnitude of particles being within the limits of 50 – 500 nm.

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