

Detonation synthesis of non-agglomerated metallic nanoparticles deposited on carbon supports

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Abstract. Synthesis of nanoparticles is carried out by thermal decomposition of organometallic complex compounds in the detonation front of explosives, where the temperature reaches several thousand degrees. The low concentration of metals in the total mass of the charge leads to the formation of single non-agglomerated nanoparticles deposited on detonation carbon. Depending on the conditions, the rounded nanosized particles of Ni, Ag, Au and Pd are formed according to the data of high-resolution transmission electron microscopy.

1. Introduction

At the detonation front of high explosives (HEs), the pressure and the temperature are reached tens of GPa and several thousand degrees, respectively. Under such conditions, a variety of chemical reactions take place and, as a result, detonation products are formed. Depending on the physical properties of the charge and especially on the chemical composition, these detonation products can be completely different. Usually, the carbon residue produced by detonation of HEs with a negative oxygen balance (detonation soot) is subjected to detailed studies. Moreover, the detonation soot contains a wide variety of forms of carbon. The characteristic features of detonation carbon are peculiar to specific explosives. It is possible to distinguish such carbon forms as nanodiamonds, ranging in size from one to hundreds of nanometers, onion-like carbon, also measuring from units to hundreds of nanometers, graphite-like fibers of various lengths and thicknesses, and amorphous carbon (e.g. [1]). At the same time, the formation of carbon particles is quite a long process compared to the typical times of the detonation process. The time of von Neumann spike for most explosives is not more than hundreds of nanoseconds. However, the authors of this work shows that the average size of the carbon particles behind the front grows during microseconds [2]. Accordingly, the final morphology of carbon can be predetermined by the researcher. Nevertheless, it is impossible to achieve the morphological homogeneity of the detonation products because of the substantial nonstationarity of the process.

Thus, the region behind the detonation front of explosives is essentially a “chemical reactor” with extremely high pressure and temperature. The use of such “reactor” for chemical processes seems to be promising.

In this paper, we consider the effect of the explosion energy on the admixtures of particles of complex organometallic compounds embedded into the explosive charge. A deep decomposition of impurity molecules with the formation of nanocrystalline metal structures is observed behind the detonation front. 15 years ago the co-authors of this work began to study on this subject [3]. Ag stearate was used there as an addition to the charge of pentaerythritol tetranitrate (PETN). The synthesized Ag particles had sizes from 3 to 20 nanometers. Later, the authors obtained nanoparticles of other metals (Bi, Co, Fe, Pb) in similar experiments [4]. It was found that the formation of nanoparticles occurs through a diffusion mechanism, but their growth is limited by the formation of a carbon shell on the surface. Therefore, as the concentration of metal atoms decreases, the concentrations of condensed carbon increases, the decrease of the size of the synthesized nanoparticles can be expected.

The formation of nanoparticles in the products of decomposition of impurities containing metals during the detonation is a fairly well-known phenomenon. Generation of metal nanoparticles during the detonation is possible for a wide range of explosives and metal-containing precursors. Thus, for the detonation of mixture of picric acid and ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$), the iron particles (predominantly ferrum oxide) were formed with sizes from 5 to 20 nanometers, covered with a rather thick layer of graphite-like carbon [5]. For the detonation of RDX with mixture of iron nitrate ($\text{Fe}(\text{NO}_3)_3$) and carbamide ($(\text{NH}_2)_2\text{CO}$), the average size of the synthesized iron particles was 55 nanometers [6]. The results described above confirm the diffusion mechanism of metal particle formation [4].

In work [7], the nanoparticles of cobalt and nickel were obtained at the detonation of PETN with additives of the solution of cobalt/nickel nitrate ($\text{Co}(\text{NO}_3)_2/\text{Ni}(\text{NO}_3)_2$) and carbamide in ethyl alcohol. Thus, cobalt particles of about 20 nanometers in size, coated with amorphous carbon, and nickel particles of 5 – 10 nm, coated with graphite-like carbon were observed. For the detonation of RDX with copper nitrate ($\text{Cu}(\text{NO}_3)_2$) and other additives that produce a carbon support, the copper nanoparticles from 10 to 30 nanometers in size were formed. This nanoparticles are also coated by a layer of carbon.

Accordingly, the formation of metal nanoparticles behind the detonation front of composite explosives is observed for a wide variety of metal-containing precursors and HEs. In all cases, the resulting metal particles (or their oxides) are covered by a layer of carbon of different morphology and thickness. There are reasons to suppose that the final particle size depends on the explosive used and both the metal itself and the additives. The lower the content of the metal atoms in the precursor, the smaller the particle size in the detonation products can be expected.

2. Experiment

In this paper, we attempt to obtain small sized metal nanoparticles by choosing the type of precursors with a low content of metals. The following precursors are used: argentum caprylate $\text{C}_7\text{H}_{15}\text{COOAg}$, tetraamminegold (III) $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$, nickel stearate (II) $\text{Ni}(\text{C}_{17}\text{H}_{35}\text{COO})_2$ and palladium stearate (II) $\text{Pd}(\text{C}_{17}\text{H}_{35}\text{COO})_2$. As a carbon supports, we use detonation carbon which synthesized during explosion of explosives with a negative oxygen balance (benzotrifuroxane (BTF) and triaminotrinitrobenzene (TATB)). The soot produced at the detonation of these explosives has been well studied [1]. Conditions behind the detonation front of these explosives and, accordingly, the morphology of detonation carbon, are significantly different. Particularly, the large spherical carbon particles with sizes up to hundreds of nanometers are typical for BTF. These particles are generated in the detonation wave as a liquid phase, but their condensation occurred in different ways, resulting in both onion-like particles up to 100 nm in diameter and porous diamonds. The TATB detonation carbon consists mainly of carbon fibers up to tens of nanometers long and particles of amorphous carbon of up to tens of nanometers in size. TATB is convenient for carrying out diffraction

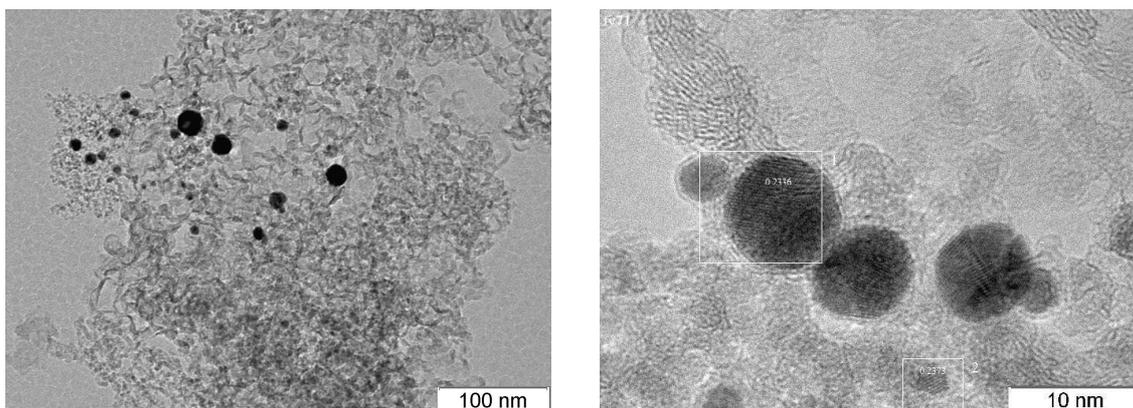


Figure 1. 3% $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ and TATB/HMX 50/50.

dynamic studies of the condensation of metallic nanoparticles, since the charges of pure TATB during the detonating process practically do not scatter x-ray beam into small angles [2]. The materials of the standard detonators and initiating systems can lead to substantial contamination of the detonation soot with impurities. Therefore, we add HMX to the charges of TATB to increase the sensitivity to a weak initiating impact. HMX does not produce significant amount of condensed carbon. Moreover, the addition of HMX in TATB in various proportions does not lead to observed changes in the process of condensation of carbon behind the detonation front [2].

Depending on the precursor and the specific explosive, the precursor is added by various ways. BTF is highly soluble in acetone. BTF precipitates if water is added into this solution. If there is a suspension of precursor in the solution, BTF can also deposit on the precursor particles. We obtain in such way the explosive composites contained argentic caprylate and nickel stearate.

Explosive composites based on TATB are made by the reverse method. The precursor solution is mixed with the TATB powder, and after the solvent evaporates, the precursor precipitates on the TATB. After that, we mixed HMX and TATB in the ratio of 50/50.

The mass fraction of precursors is no more than 3%. Such small concentrations weakly affect on the detonation parameters of the HEs, as well as this allow us to expect small-sized nanoparticles in final products because of the concentration of metal atoms are low.

These explosive compositions are pressed as cylindrical charges of diameter of 20 mm and of density of 1.7–1.8 g/cc. The initiation system and the conditions of experimentants are the same as in [1]. The entire experimental assembly is frozen into ice shell. As the initiator of detonation, the powder charge of PETN is used. Condensed detonation products mixed with water and crushed ice are collected, dried and then studied by transmission electron microscopy (TEM) facility.

The TEM images for the TATB/HMX 50/50 and 3% $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ sample are shown in figure 1. According to the TEM data, the rounded gold nanoparticles from 2 to 25 nanometers in size, covered with a layer of carbon, are observed. For all samples the deposition of nanoparticles on detonation carbon is nonuniform. This can be caused by insufficient homogeneity of mixing of the initial components, as well as by a low concentration of the precursor. The distribution of the nanoparticles in size is polydisperse, moreover, a tendency for agglomeration of individual particles into clusters take place.

The second sample is based on BTF contains 2% $\text{C}_7\text{H}_{15}\text{COOAg}$. For this sample the rounded silver nanoparticles with polydisperse size distribution from 2 to 60 nanometers is

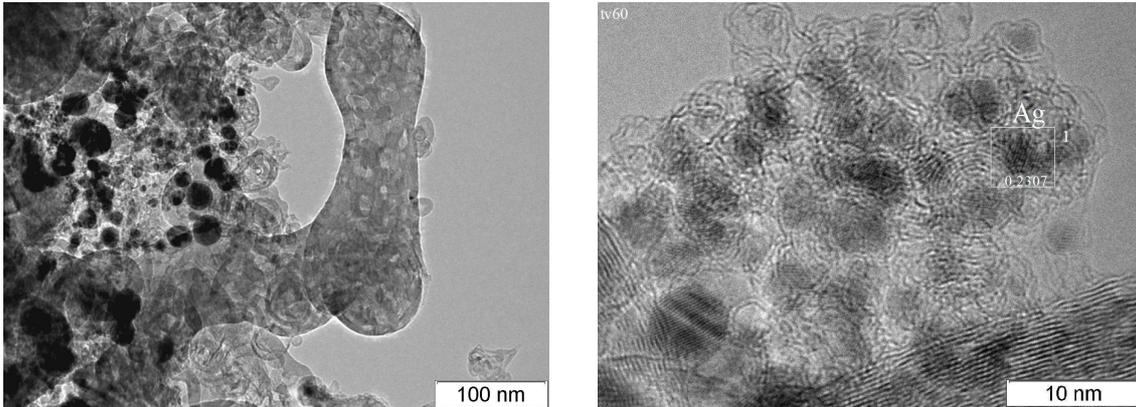


Figure 2. 2% $C_7H_{15}COOAg$ and BTF.

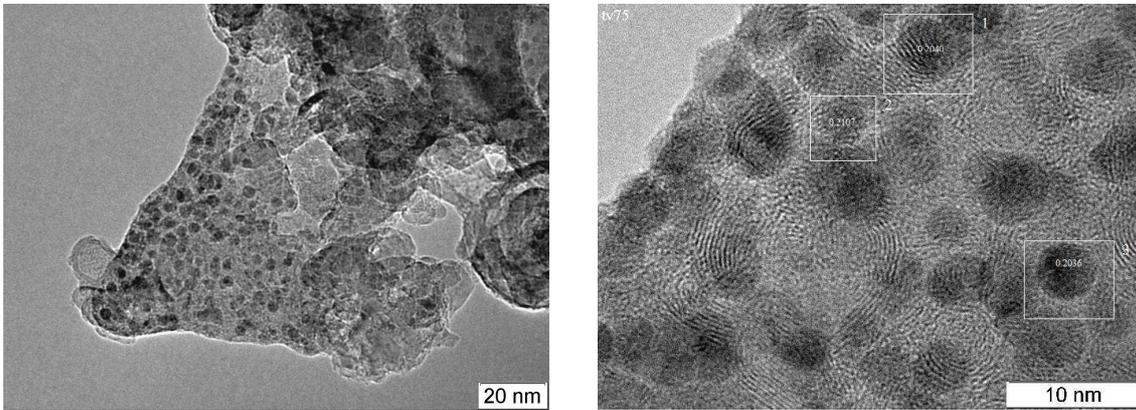


Figure 3. 3% $Ni(C_{17}H_{35}COO)_2$ and BTF.

observed (figure 2). These nanoparticles are mainly larger than in work [3], this is possibly because of a higher argentine content in the precursor molecule. The high tendency to agglomeration into the clusters the most of particles are observed. For this argentine contained precursor, the largest nanoparticles are obtained. The morphology of the carbon support is typical for the detonation soot of BTF.

For the third sample also based on BTF with the addition of 3% $Ni(C_{17}H_{35}COO)_2$, a practically monodisperse size distribution of nanoparticles is observed (figure 3). These nanoparticles from 3 to 5 nm in size and they are in the non-agglomerated state. The oxygen balance of this explosive composite is negative, therefore, probably, the formation of metallic particles takes place at the begin. Later, they oxidizes at the preparation of detonation products for microscopic study.

The minimal mean size of the synthesized metal nanoparticles obtained for the fourth sample containing 2.5% $Pd(C_{17}H_{35}COO)_2$ and TATB/RDX 50/50 is found. The TEM image and the histogram of the nanoparticle size distribution according to the TEM data are shown in figure 4. The mean size of nanoparticles practically coincides with the average volumetric-surface value $d_s = \sum d_i^3 / \sum d_i^2$ and with weight-average value $d_s = \sum d_i^4 / \sum d_i^3$. This indicates that the most amount of palladium is contained in nanoparticles of sizes of about 1.7 nm.

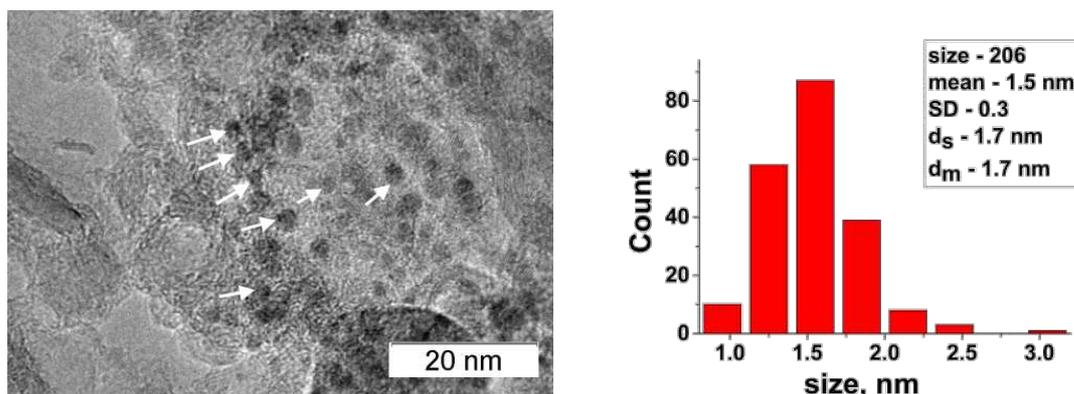


Figure 4. 2.5% Pd(C₁₇H₃₅COO)₂ and TATB/HMX 50/50.

3. Conclusions

For a wide set of the metal-containing precursors embedded into the charges of various HEs, the metal nanoparticles deposited on the detonation soot are observed. Depending on the compound of the initial explosive composition, the nanoparticles from one to tens of nanometers or more in size are formed. In all the cases this nanoparticles are covered by a layer of carbon. According to our data, Au and Ag nanoparticles have a tendency to agglomerate into clusters; for Ni and Pd nanoparticles such behavior is not typical. Moreover, nanoparticles obtained from samples containing Au and Ag have a wide size distribution, however the size distribution of Ni and Pd nanoparticles is close to monodisperse. The mean size of the nanoparticles is determined by the length of the additive molecule (the content of the metal atoms in the additive), the choosed metal and the explosive. The choice of HE also determines the morphology of the carbon support. The smallest mean size of nanoparticles obtained by the detonation synthesis nanoparticles is 1.5 nanometers.

References

- [1] Kashkarov A O, Prueel E R, Ten K A, Rubtsov I A, Gerasimov E Yu and Zubkov P I 2016 *Journal of Physics: Conference Series* **774** 012072
- [2] Ten K A, Titov V M, Prueel E R, Kashkarov A O, Tolochko B P, Aminov Yu A, Loboyko B G, Muzyrya A K and Smirnov E B 2014 *Proceedings Fifteenth International Detonation Symposium. Publication No. ONR-43-280-15* (San Francisco, CA) pp 369–74
- [3] Ancharov A I, Zubkov P I, Ivanov P I, Kartashov A M, Lukyanchikov L A, Svih V G, Ten K A, Tolochko B P and Sharafutdinov M R 2003 *Proceedings of the International Conference "V Khariton's Topical Scientific Readings"* ed Mikhailov A L (VNIIEF, Sarov) pp 141–4
- [4] Tolochko B P, Chernyshev A P, Ten K A, Prueel E R, Zhogin I L, Zubkov P I, Lyakhov N Z, Luk'yanchikov L A and Sheromov M A 2008 *The Physics of Metals and Metallography* **105** 134–140
- [5] Lu Y, Zhu Z and Liu Z 2005 *Carbon* **43** 369 – 374
- [6] Luo N, Liu K, Liu Z, Li X, Chen S, Shen Y and Chen T 2012 *Nanotechnology* **23** 475603
- [7] Luo N, Li X J, Wang X H, Mo F and Wang H T 2010 *Combustion, Explosion, and Shock Waves* **46** 609–613