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Characterization of the condensed carbon in detonation soot

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Abstract

A number of pure and composite explosives with a negative oxygen balance were detonated in a hermetic steel chamber under different environmental conditions. After detonation, solid carbonaceous products (detonation soot) and ultrafine diamond separated from the soot were collected for examination. Elemental analysis, high resolution transmission electron microscopy, X-ray diffraction, Raman spectroscopy, Fourier-IR, X-ray photoelectron spectroscopy and small angle X-ray scattering were used to characterize the structure, composition and surface properties of the condensed carbon in the soot. Crystallite size and microstrain of ultrafine diamond and the graphitization index of the graphite phase were calculated according to XRD patterns. The yields of the soot and ultrafine diamond from the explosives were obtained. The influences of charge conditions and environmental conditions on the formation mechanisms and properties of condensed carbon were analyzed. Detonation soot contains ultrafine diamond, graphite and amorphous carbon. Two types of graphite structures were present in the detonation soot.

Keywords: A. Soot; Diamond; Graphite; D. Microstructure

1. Introduction

The study of the formation of condensed carbon and its influence on detonation has long been a focus in detonation physics. Conventionally the condensed carbon in detonation soot was regarded as bulk graphite. Mader [1] extensively used a graphite equation of state to calculate the detonation properties of a variety of explosives. The study of the synthesis of ultrafine diamond (UFD) by explosive detonation has intrigued this research and deepened our understanding in this regard. The study of detonation-synthesized ultrafine diamond first appeared in the late 1980s and quickly developed in several scientific centers [2–4]. Mass production of the UFD has been reported and application fields are emerging that are distinct from those of normal diamond, for example, as a seeding material of CVD diamond films [5] and as an undoped low-field electron emission material [6]. However, the mechanism of carbon condensation in the detonation process still remains controversial at present.

The formation of condensed carbon and its evolution during detonation are very important to understand the detailed physical and chemical picture of detonation. They can also enrich our understanding of some detonation phenomena such as the detonation build-up of some carbon-rich explosives. At present it is still very difficult to directly measure the compositions and phase evolution of detonation products during detonation, because of the extremely high temperature, high pressure and short duration. Close examination of the detonation soot after the expansion and cooling of detonation products may help us improve our understanding of carbon condensation and carbon equations of state in detonation calculations. In addition, the characterization of the condensed carbon is very important for the application of the detonation soot and ultrafine diamond. Greiner et al. [7] have done extensive studies in the chemistry of detonation soot. The present paper presents generalized results of the characterization of condensed carbon in the detonation soot conducted in our laboratory.

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2. Experiment and analysis

Explosive charges were detonated in a hermetic steel chamber with a volume of about 1.6 m^3. The charge mass was ~200 g. To evaluate the influences of explosive compositions on the formation of condensed carbon, a variety of explosives and different organic additives were used. The explosives used included trinitrotoluene (TNT), hexogen (RDX), nitroguanidine (NQ), nitromethane (NM), Tetryl, desensitized PETN and PBX8701. Among them, TNT was the most widely used component because of its high content of carbon. The organic additives included diesel oil, dinitronaphthalene and polyethylene. Environmental conditions influence the expansion and cooling process of detonation products and then may influence the formation of carbon phases and their interaction. To evaluate the influences of environmental conditions, the chamber was filled with different gases including N_2, Ar, CO_2 and air, or else the charges were immersed in water, or wrapped by ice or pyrolytic salts including NH_4HCO_3 and $NaHCO_3$ before detonation.

After detonation, the black detonation soot was collected and dried at 110 °C to constant weight for examination. In some cases, ultrafine diamond was separated from the detonation soot by acid oxidation for further examination. The methods used to purify the UFD have been described previously [8]. The soot was first soaked in aqua regia for 5–10 h to remove metallic impurities and part of the amorphous carbon. After decanting, different oxidizing agents including perchloric acid, a mixture of nitric acid and sulphuric acid, and a mixture of sulphuric acid and $KMnO_4$ were added and refluxed with stirring for enough time until the color of solution changed from black to light brown. The powder was then thoroughly washed with distilled water and dried in vacuum. The results showed that, when a mixture of sulphuric acid and $KMnO_4$ was used, the cost of purification can be noticeably reduced by 50%, compared with that by perchloric acid. Then the detonation soot and ultrafine diamond were weighed to obtain their yields from the explosives, i.e. wt.% of total charge.

The soot and ultrafine diamond were studied by use of various techniques including elemental analysis, X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering, high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Raman spectroscopy and Fourier-IR (FTIR). XRD study was carried out on a Rigaku Dmax-2400 diffractometer using Cu Kα irradiation. HRTEM was performed on a H9000 electron microscope with accelerating voltage of 200 kV, in which powder samples for investigation were placed on special grids with a cell size of 20 μm. Raman spectra were measured on a Renishaw-RM1000 microscopic confocal Raman spectrometer with the 514.5-nm line of an argon ion laser. The IR spectra of the samples in KBr pellets were collected on a PE-1760 FTIR spectrometer.

3. Results and discussion

3.1. High resolution transmission electron microscopy

HRTEM analysis demonstrated that various solid carbon phases were present in the detonation soot. Fig. 1 shows some results of the detonation soot of pure TNT under water environmental conditions. Fig. 1a shows that many ribbon-like graphite particles are highly curved and tangled together with the presence of some diamond particles. The (002) planes of graphite with an interlayer spacing of 0.335 nm and the (111) planes of diamond with a spacing of 0.205 nm can be observed. The (002) planes of graphite were highly curved, which may be mainly due to the extremely high pressure of the detonation process [9]. The pressure generated by explosive detonation is generally very high (20–30 GPa) and the duration of high pressure is very short (10^{-6}–10^{-7} s), driving the detonation products to expand at a high velocity of over 1 km/s. This may cause the curvature of the graphite ribbons along with the (002) planes. Fig. 1b shows a carbon sphere whose shells are also approximately spaced by 0.33 nm, revealing that the carbon sphere is composed of defect closed graphite shells. The size of the carbon sphere was similar to that of diamond particles. Onion-like carbon spheres were also reported by Kuznetsov et al. [10] and Mal'kov et al. [11]. Recent experiments [12] demonstrated that the UFD can be easily converted to carbon onions at 1800 K, as diamond-to-graphite phase transition initiates on {111}-faceted surfaces. Thus it is reasonable to assume that carbon spheres were graphitized products of the UFD during the expansion of detonation products. Most diamond particles in the soot exhibited spherical or quasi-spherical shapes, as shown in Fig. 1c. This special morphology was also observed by Greiner et al. [3] and Mal'kov et al. [11] and may be explained by the formation of UFD through a liquid state. However, occasionally diamond particles with regular cubiform or polyhedral shapes can also be found, as shown in Fig. 1d. Similar results were also reported by Saha et al. [13] recently. Further studies are needed to clarify this phenomenon.

Diamond particles in the above-mentioned soot of TNT had a uniform size of 4–7 nm. However, apparently two different sizes of diamond particles were present in the detonation soot of explosive mixtures, for example TNT/RDX (50/50) in a water environment. The larger particles had a size of 10–20 nm, and the smaller ones 4–7 nm. This may be explained as the detonation products of individual explosive components in explosive mixtures did not totally mix with each other.

HRTEM analysis also showed that some larger diamond particles were covered by a mantle of graphite shells. It is reasonable to speculate that graphite ribbons were crystallized directly from free carbon and had a good crystallite structure. During the expansion and cooling of detonation products, some diamond particles were totally graphitized

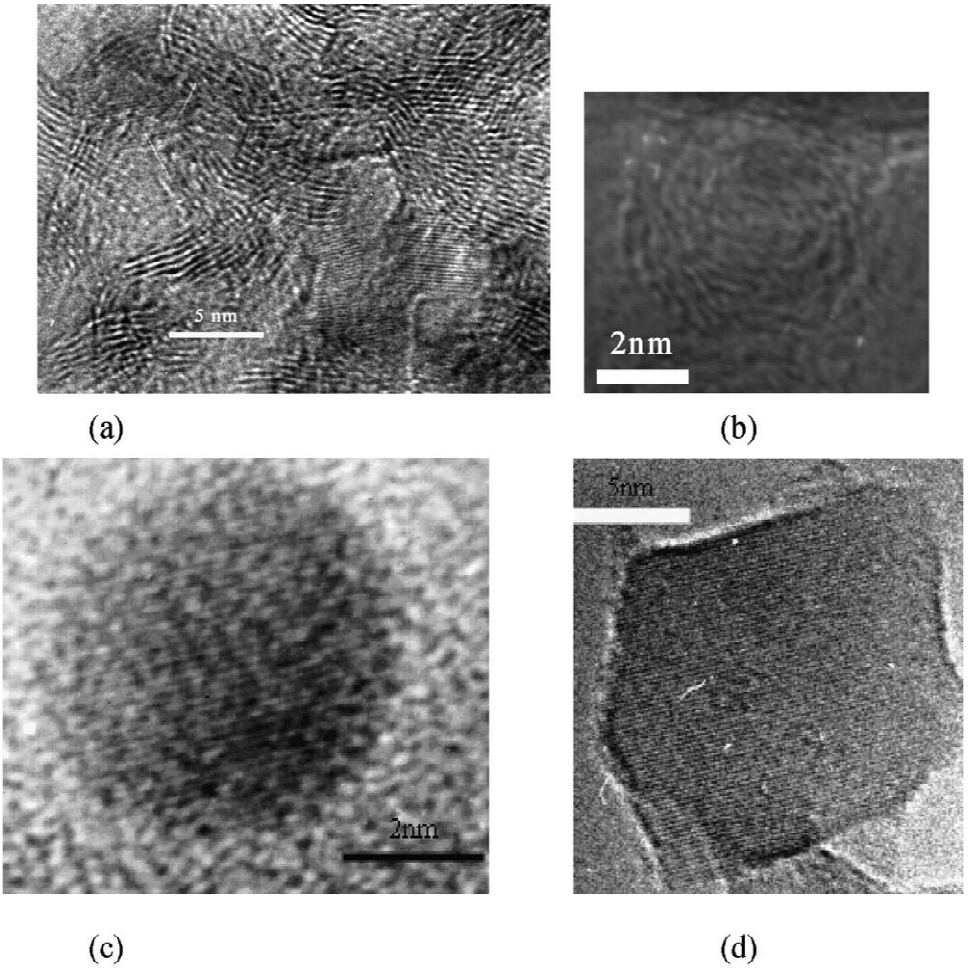

Fig. 1. HRTEM images of condensed carbon in the detonation soot of TNT in a water environment: (a) tangled graphite ribbons and diamond; (b) carbon sphere; (c) spherical diamond particle; (d) polyhedral diamond particle.

and converted into onion-like carbon spheres, and some were partially graphitized and formed mantels outside diamond particles. HRTEM examination also revealed that a lot of amorphous carbon was present in the detonation soot. Diamond, graphite ribbons, onion-like carbon spheres were all in nanometer sizes. This can be explained as carbon particles did not have enough time to grow into larger sizes due to the inherent short duration of the detonation process.

3.2. Elemental analysis and XPS

Charge conditions and environmental conditions influenced the elemental composition of the soot. According to elemental analysis, the soot obtained by the detonation of TNT/RDX (50/50) in a N_2 environment contained: C ~92.2%; O ~4.4%; N ~2.5%; H ~0.5%; and a small fraction of Fe, S and other impurities. XPS analysis showed that the diamond phase accounted for ~12% of the soot, while the graphite phase accounted for ~71%. After purification by use of perchloric acid, the UFD contained: C ~87.5%; H ~0.5%; N ~1.6%; and O ~10.2%. XPS analysis showed that ~83% of carbon atoms of the UFD were in the form of sp^3, ~5% in sp^2, and ~12% in C–H, C–O and C–N, suggesting that some unbonded carbon atoms on the surface of the UFD were saturated by N, H and O atoms. The increase of oxygen content and decrease of carbon content after purification were due to the oxidation during purification. Environmental conditions played an important role in the formation of condensed carbon. When previous TNT/RDX (50/50) charges were detonated in a vacuum, no diamond was obtained. Their soot contained: O ~48.2%; C ~32.8%; N ~2.1%; and H ~0.4%. XPS analysis showed that most carbon atoms of the soot were in the form of sp^2, C–C chains, or C–H, C–O and C–N. It was clearly shown that after purification,

the UFD still contained oxygen, nitrogen and hydrogen. FTIR analysis showed that a lot of functional groups were present on the surfaces of UFD particles (Fig. 4), resulting in a decrease of carbon content in the UFD. SAXS analysis showed that the grain size of UFD obtained under different charge conditions and environmental conditions was in the range of 1–20 nm and the average grain size was 4–6 nm, which was consistent with HRTEM results. The specific area of UFD particles was in the range of 380–420 m^2/g.

3.3. X-ray diffraction

Fig. 2a shows the XRD pattern of the soot obtained by the detonation of pure TNT in a water environment and soaked in aqua regia for 0.5 h. The peak around $2\theta = 26°$ corresponds to graphite (002) diffraction. A weak peak around $2\theta = 43.6°$ corresponding to diamond (111) diffraction could also be observed. The intense background of the XRD pattern reveals the presence of considerable amorphous carbon. Fig. 2b shows the XRD pattern of the soot of a mixture of TNT/diesel oil (50/2.4) in a water environment without any pre-processing. A weak peak around $2\theta = 43.6°$ demonstrates the presence of diamond phase in the soot. Fig. 2c shows the XRD pattern of the soot obtained by the detonation of TNT/RDX (50/50) in a water environment and soaked in aqua regia for 2 h. Both the graphite (002) diffraction peak and the three peaks corresponding to diamond (111), (220) and (311) diffraction can be clearly observed, demonstrating that the content of diamond in the soot of TNT/RDX (50/50) was higher than that of pure TNT. Fig. 2d shows the XRD patterns of UFD obtained by the detonation of TNT/RDX

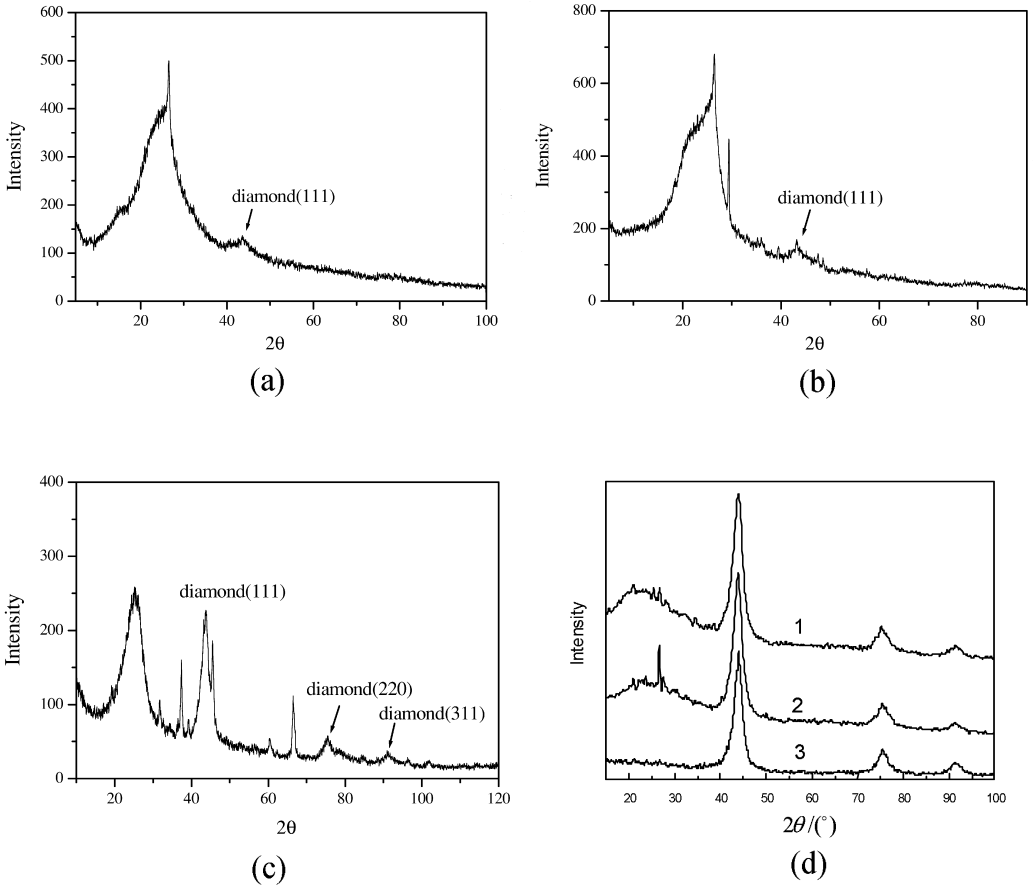

Fig. 2. XRD patterns of the soot and UFD: (a) soot of pure TNT in water environment; (b) soot of TNT/diesel oil (50/2.4) in water environment; (c) soot of TNT/RDX (50/50) in water environment; and (d) UFD obtained by the detonation of TNT/RDX (50/50) under different environmental conditions (1, N_2; 2, NH_4HCO_3; 3, water) and purified by perchloric acid under the same conditions.

Table 1
Grain size and microstrain of the UFD obtained by the detonation of TNT/RDX (50/50) under different environmental conditions and purified by perchloric acid under the same conditions

Environmental conditions	Average deviation of lattice constant (%)	Average size of crystallite (Wilson method) (nm)	Microstrain (%)
N_2	+0.25	4.2	0.6381
NH_4HCO_3	+0.09	3.7	0.410
Water	+0.24	6.6	1.004
Ice	+0.02	4.0	0.1338

(50/50) under different environmental conditions including N_2, NH_4HCO_3 and water. The UFD was purified by perchloric acid under the same conditions. Three characteristic diffraction peaks of diamond demonstrate that the UFD had a cubic conformation. The three peaks have considerable width due to the small size effects of the UFD. A minor peak at around $2\theta = 26°$ (see curve 2) and broad diffraction bands at the range of $2\theta = 20–30°$ (see curves 1 and 2) demonstrate the presence of graphite and amorphous carbon after purification. Fig. 2d also shows that the UFD obtained in a water environment contained less impurities than those obtained under other environmental conditions.

XRD patterns can also be used to calculate the average grain size, average deviation of cell parameters and microstrain of the UFD by mixing the UFD powder with high-purity silicon powder as an inner standard, according to conventional procedures. As indicated in Table 1, the UFD was characterized by having considerable microstress and larger crystal lattice parameters than bulk diamond. Such a high level of lattice deformation can be explained either by the inhomogeneous deformation of the UFD particles during the strongly nonequilibrium detonation process, or by the effects of other inserted atoms in the crystal lattice. The values of microstress did not change noticeably when the UFD was heated up to 1000 °C in Ar atmosphere, which can be explained by the high potential barrier hindering the annealing of defects. In the above-mentioned environmental conditions, the UFD obtained in a water environment had the largest particle size and the largest microstrain at the same time. Among all the environmental conditions, water can generate the highest cooling rate, resulting in the largest microstrain in the UFD samples obtained in a water environment.

A graphitization index reveals the crystallite perfection of graphite. The average interlayer spacing d_{002} of graphite can be obtained through calculating the XRD pattern, and then the graphitization index can be obtained by comparing the measured d_{002} value with the theoretical d_{002} value 0.3348 nm. Table 2 shows the graphitization indexes of the graphite phases in the soot and the graphite residue in the UFD after purification. The graphitization indexes of the soot obtained under different environmental conditions were different, and the graphitization indexes before and after purification were also different. Thus it is reasonable to assume that the structure of graphite residue in the UFD was different from that of the graphite in the soot. We speculate that the graphite residue in the UFD corresponded to the graphite mantles outside the diamond particles. Graphite ribbons were easier to remove through oxidation, while the graphite mantles were more difficult to totally remove because part of the graphite atoms were trapped by the diamond lattice.

3.4. Raman spectra

Fig. 3a shows the Raman spectra of the detonation soot and the UFD obtained by the detonation of TNT/RDX (50/50) in a water environment. The UFD was purified by perchloric acid. The Raman spectrum of high-purity electrode graphite is given for comparison. Two broadened Raman peaks of the soot (curve b) corresponding to the characteristic D peak and G peak of graphite were observed at ~1352 cm^{-1} and 1575 cm^{-1}. Though the three characteristic XRD peaks of diamond in the soot were clearly observed (Fig. 2c), the characteristic Raman peak of diamond cannot be observed in the Raman spectra of the soot, because the scattering area of diamond is only about 1/60 of that of graphite [14].

The graphite Raman peaks of the soot had a consider-

Table 2
Graphitization indexes of the graphite phases in the soot and the graphite residue in the UFD after purification. The soot was obtained by the detonation of TNT/RDX (50/50) in ice and nitrogen environments and purified by perchloric acid under the same conditions

Graphitization index	Ice		N_2	
	Before oxidation	After oxidation	Before oxidation	After oxidation
Franklin index	0.74	0.01	0.92	0.32
Bacon index	0.78	0.06	0.93	0.41

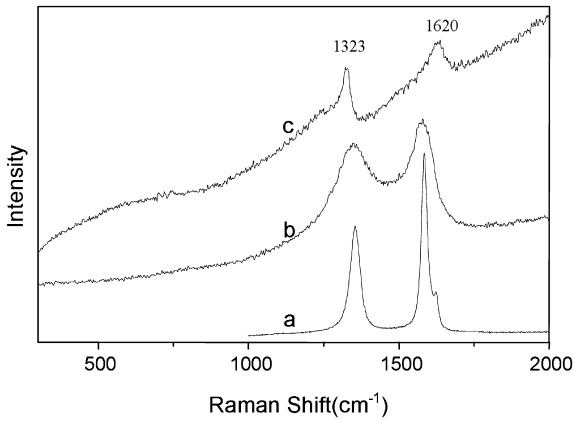

Fig. 3. Raman spectra of the detonation soot and UFD of TNT/RDX (50/50) in a water environment. The UFD was purified by perchloric acid. The Raman spectrum of high-purity electrode graphite is superposed for comparison. (a) High purity electrode graphite; (b) detonation soot; (c) UFD.

able width compared with those of high purity electrode graphite, demonstrating that the graphite in the soot was not highly ordered. The intensity ratio I_d/I_g (I_d and I_g refer to the intensity of D peak and G peak, respectively) of curve b was up to 0.91, revealing that the graphite crystallites in the soot were quite small.

The Raman peaks of the UFD assigned to sp^2 and sp^3 carbon were observed at ~1620 cm^{-1} and 1323 cm^{-1}, respectively (curve c), suggesting that the UFD contained a small amount of sp^2 carbon. The broad Raman band at around 400–700 cm^{-1} was assigned to amorphous carbon. The Raman band assigned to sp^3 carbon was asymmetric with a shift of -8.9 cm^{-1} and a linewidth of 30.4 cm^{-1}.

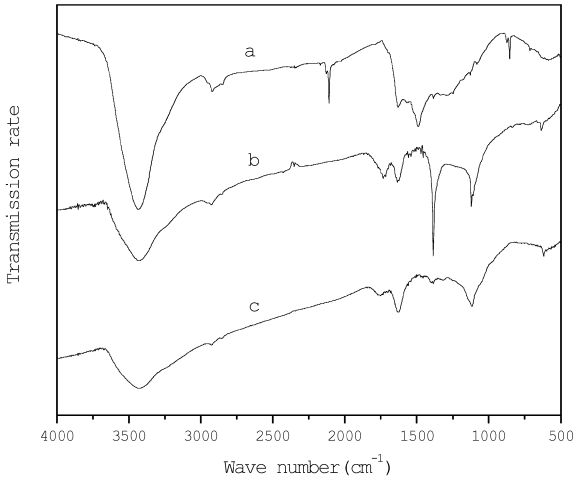

Fig. 4. FTIR spectra of the soot of TNT/RDX (50/50) in a water environment (curve a), the UFD purified by perchloric acid (curve b), and the UFD purified by a mixture of sulphuric acid and $KMnO_4$ (curve c).

Considering the difference between the scattering areas of diamond and graphite, the content of sp^2 carbon residue in the UFD was less than 1%, close to 2% estimated by Yoshikawa et al. [15].

The grain size of UFD can be estimated according to the half-peak width and the peak shift. The results showed that the grain size of UFD was about 2–3 nm [16], smaller than that calculated by XRD patterns. If the effects of internal stress on the peak shift and peak broadening are taken into consideration, the actual grain size is larger than 2–3 nm.

3.5. FTIR analysis

FTIR analyses were carried out to explore the surface functional groups of the soot and UFD. Fig. 4 displays some results of FTIR spectra, in which curve a denotes the soot obtained by the detonation of TNT/RDX (50/50) in a water environment and soaked in aqua regia for 2 h, curves b and c denote the UFD purified from the soot by perchloric acid and a mixture of sulphuric acid and $KMnO_4$, respectively. The results showed that the surfaces of both the soot and the UFD were covered to a large extent with carbonyl, carboxyl, methyl and nitryl groups. Differences can also be observed between the spectra of the soot and UFD, and between the UFD purified by different methods, demonstrating that the surface properties of UFD were influenced by oxidation. Further analyses also showed that charge conditions and environmental conditions can affect the type and number of functional groups on the surfaces of soot and UFD. The presence of surface functional groups makes it possible to chemically modify the soot and UFD and use them for the preparation of new types of materials, absorbents and catalysts. These functional groups may also cause the deviation of the lattice parameter and the density of UFD from the corresponding values of normal diamond crystals.

3.6. Yields of soot and UFD

Extensive experiments were done to evaluate the influences of charge conditions and environmental conditions on the yields of soot and UFD. Explosive compositions determine not only the total amount of excess carbon involved in carbon condensation but also the pressure and temperatures generated in detonation, which in return affect the yields of soot and UFD. To obtain a high yield of soot, explosive charges should have a high content of carbon, which can be achieved by selecting carbon-rich explosives such as TNT and Tetryl, or by adding some organic materials such as diesel oil and polyethylene. In addition, the formation of diamond requires certain high pressure and temperatures, which can be achieved by adding some explosives with high detonation pressure and temperatures such as RDX. A wide range of explosive mixtures were investigated in the experiments. Partial results are listed in Table 3. The results showed that the

Table 3
Yields of the detonation soot and UFD under different charge conditions

	TNT	RDX	TNT/RDX (70/30)	TNT/RDX (50/50)	TNT/RDX (50/50)	NQ/RDX (50/50)	NM/RDX (40/60)
Environmental conditions	N_2	N_2	N_2	Water	N_2	Water	Water
Detonation soot (%)	27.2	8.0	21.0	21.9	18.0	8.7	24.1
UFD (%)	2.8	1.1	7.5	9.1	3.5	0.4	0.3

Table 4
Yields of the detonation soot and UFD of TNT/RDX (65/35) under different environmental conditions

	N_2	Water	Ice	NH_4HCO_3
Detonation soot	19.0	21.0	22.0	NA
UFD	4.5	9.1	8.7	6.0

yields of the soot and UFD were largely affected by the explosive compositions. Among all the explosive mixtures used, TNT/RDX mixtures can produce the highest yield of UFD. Ideal compositions of TNT/RDX mixtures for the synthesis of UFD were TNT 50–70%, RDX 50–30%.

Organic additives may increase the carbon content, however they may also decrease the detonation pressure and temperatures, resulting in a decrease of UFD yields. The results showed that the addition of organic additives did not increase the yields of UFD as expected. For example, detonation of TNT/diesel oil (50/2.4) in a water environment can generate a soot yield of 31.3%, however the yield of UFD was less than 1.0%.

The environmental conditions influence the expansion and cooling of detonation products, thus influence the duration of crystallization, the oxidation of carbon and the graphitization of diamond. Experimental results showed that the yields of soot and UFD were strongly influenced by the environmental conditions. For example, when TNT/RDX (50/50) charges were detonated in vacuum, the yield of soot was 7%, however nearly no diamond was obtained. However when they were detonated in a water environment, a soot yield of 21.9% and a high UFD yield of 9.1% can be obtained. Table 4 illustrates the influences of environmental conditions on the yields of soot and UFD. Among all the environmental conditions used, water can produce the highest yield of UFD.

4. Conclusions

The condensed carbon in the detonation soot has a complex composition. It is made up of clusters of diamond, graphite and amorphous carbon, all of which are in nanometer sizes. The cluster sizes are small enough to have significant surface contributions. The UFD has a cubic conformation, consisting mostly of single crystals. Two types of graphite phases are present in the detonation soot. One is tangled and highly curved graphite ribbons, the other is carbon spheres and carbon mantles graphitized from the UFD. The UFD contains a large number of defects and considerable microstrain. Both charge conditions and environmental conditions influence the elemental composition of the soot, the yields of the soot and UFD, and the grain size and the microstrain of UFD. The soot and UFD are covered to a large extent with surface functional groups. The surface properties of UFD are influenced by purification methods.

Acknowledgements

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References

[1] Mader CL. In: 2nd ed, Numerical modeling of explosives and propellants, New York: CRC Press; 1998, pp. 33–52.
[2] Staver AM, Gubareva NV, Lyamkin AI, Petrov EA. Fizika Goreniya i Vzryva 1984;20(5):100–4.
[3] Greiner NR, Philips DS, Johnson JD, Volk F. Nature 1988;333:440–2.
[4] Yamada K, Sawaoka AB. Carbon 1994;32(4):665–73.
[5] Chen PW, Ding YS, Chen Q, Huang FL, Yun SR. Diamond Relat Mater 2000;9:1722–5.
[6] Zhu W, Kochanski GP, Jin S. Science 1998;282(20):1471–3.
[7] Greiner NR, Rogers YC, Spall WD. LA-UR92-374.
[8] Chen P, Yun S, Huang F, Chen Q, Tong Y. J Funct Mater 2000;31(1):56–7.
[9] Xu T, Zhao J-z, Xu K. J Chin Electron Microsc Soc 1998;18(4):438–42.
[10] Kuznetsov VL, Chuvilin AL, Moroz EM, Kolomiichuk VN, Shaikhutdinov SK, Butenko YU. Carbon 1994;32(5):873–82.
[11] Mal'kov IY. Fizika Goreniya i Vzryva 1993;29(5):93–6.
[12] Kuznetsov VL, Chuvilin AL, Butenko YV, Mal'kov IU, Titov VM. Chem Phys Lett 1994;222:343–7.
[13] Saha DK, Koga K, Takeo H. Surf Sci 1998;400:134–9.
[14] Wada N, Solin SA. Physica B 1981;105:353–8.
[15] Yoshikawa M, Mori Y, Obata H, Maegawa M, Katagiri G, Ishida H et al. Appl Phys Lett 1995;67(5):694–6.
[16] Chen P, Yun S, Huang F, Chen Q, Ma F. Chin J High Press Phys 1999;13(1):59–63.