Физика твердого тела, 2004, том 46, вып. 4

Synthesis Mechanism and Technology of Ultrafine Diamond from Detonation

© Huang Fenglei*, Tong Yi, Yun Shourong

The National Key Laboratory of Explosion and Safety Science, Beijing Institute of Technology,
100081 Beijing, China

Ultrafine diamond (UFD) is a hybrid product of explosion mechanics and material science. In this paper, we established the synthesis mechanism of UFD, built the direct-simulation Monte-Carlo computing method for the generating of liquid drops from free carbon through coagulating in detonation, and constructed the computing programs for explosion thermodynamics conditions and phase-transition dynamics. The synthesis and purification technology were studied systemically.

1. Introduction

Ultrafine Diamond (UFD) is formed from the un-oxidized carbon in the negative oxygen balance explosive at high pressure and high temperature produced in detonation. The analysis by SAXS and TEM has shown that the particle size distribution mainly is 1–60 nm, and the median size (D_{50}) is 9–11 nm. It possesses some properties of natural diamond, simultaneously possesses some properties of nano-metric particle. This perfect combination constructs its special quality, which is different from the traditional man-made diamond and natural diamond. Its bright prospect has been predicted in the field of material science, material surface improving, and even in medicine [1]. A lot of research work about it has been done in some countries include Russian [2], Japan and America. Some research results have already put into commercial use. In China several institutes and universities are doing the related research. Beijing Institute of Technology is one of them, in which a research group started the systematic research in 1990. Here is a partial research work of ours.

2. Synthesis mechanism of UFD

In the detonation process of negative oxygen balance explosive, free carbon was released, and then turn into UFD, to which mechanism scholars have different viewpoints. They could not decide that UFD was formed in which section of detonation process involving leading shock wave (Von-Neumann peak), chemical reaction zone (ended in the point CJ) and Taylor zone (Fig. 1). Most of the scholars put up with their mechanism only by theory analysis or experiment and necessary calculation is neglected [3]. In this paper, we managed to find the forming mechanism of UFD by quantitative calculation.

2.1. The section of leading shock wave. The molecular calculation shows that the wave front energy can focus several electron volts of energy on the bands of the explosive molecule in 10^{-10} second and the energy is enough to break the molecular bonds. This splitting only occurs at the local „hot spots“. The explosive molecule absorbs the energy from the splitting at first, then breaks into individual atoms, free radicals and fragments of molecules, in which the free carbon is included.

2.2. The section of chemical reaction. At the „hot spots“, the decomposed components of the explosive are reunited, and release chemical energy, which make the temperature rise and lead to decomposition and reaction of explosive. Consequently, the chemical energy impels the leading shock wave move forward continually. As the oxygen is deficient, a part of carbon in the explosive is left and become free carbon after the detonation reaction. When the free carbon collide each other in the reaction zone, the liquid state carbon will coagulate to bigger drop and the solid state carbon will depart away again after the colliding. In traditional carbon phase plot, the temperature and pressure of the detonation should sit in the solid zone. We found that the melt point of carbon particles has relation with the particle size, for instance, the melt point of nanometer metal particles is lower than the block metal. On the basis of former researcher's work and by means of thermodynamics relations, we have a relation between the melt point (T) and the ultrafine particle size (r_s) as follows:

$$1-\theta=\frac{2}{\rho_s \Delta H_m r_s}\left[\gamma_s-\gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right], \qquad (1)$$

here $\theta = T/T_m$, T_m — the melt point of block material, ΔH_m — the melt enthalpy of the solid, ρ — density, γ — surface tension, subscribe s — solid phase, subscribe

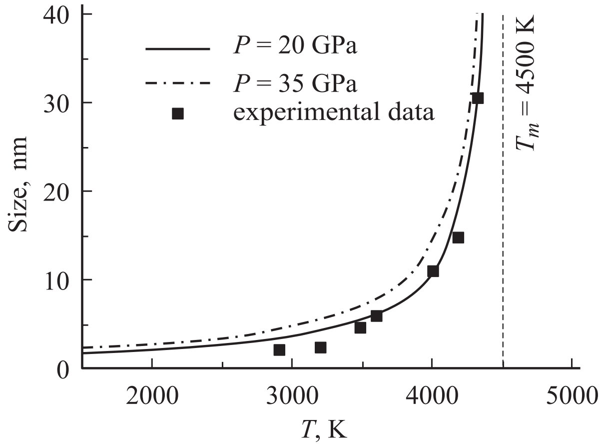

Figure 1. The relation between melt points and the size (r_s) of UFD.

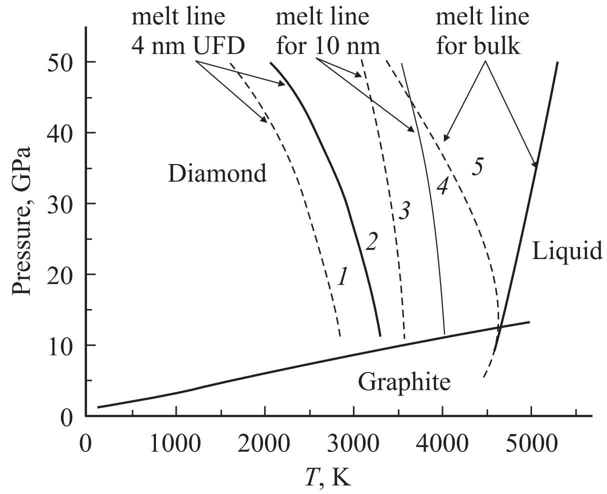

Figure 2. The phase graph of block diamond and UFD (4 nm, 10 nm). Explosives: *1* — TNT, *2* — TNT / RDX 60 / 40, *3* — RDX, *4* — PETN, *5* — BTF.

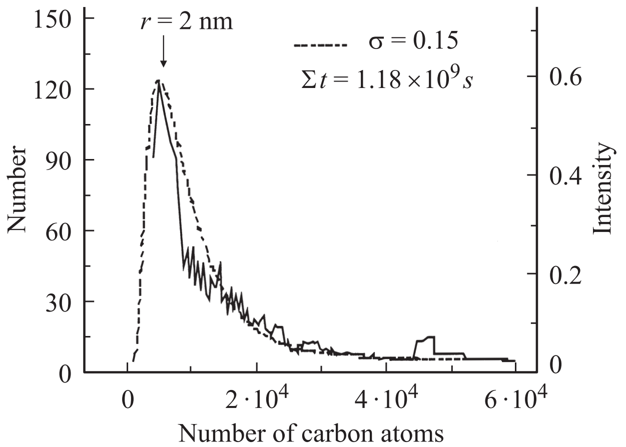

Figure 3. The distribution of the particle size at 1.18×10^{-9} second.

l — liquid phase. The above formula is that the one order Tailor Formula. Put the related parameters of diamond into formula (1), we find that the pressure only has a little influence on the melt point, but the influence of the particle size is bigger (shown in Fig. 1). When the size is less than 10 nm, the melt point decreased rapidly. It can be explained as that when the free carbon collide and coagulate to make the drop bigger the melt point is higher until it arrives the detonation temperature (T_{CJ}). In the Fig. 2, the CJ locations of five explosives are given. It is clear that the CJ location of the TNT60 / RDX40 explosive is sited in the liquid phase zone, which indicate that the free carbon from this explosive could coagulate to bigger drops.

The colliding and coagulating of the free carbon can be described by the Smoluchowski equation [4], which can be solved by Direct Simulation Monte-Carlo. For this purpose, we worked out a computing program by the „C language" and passed the test of analytic solution of Smoluchowski equation.

The calculating results by DSMC program are as follows.

1) The number of atom in the original cluster has a little influence on the coagulating.

2) The numerical calculation results is shown in the solid line in the Fig. 3. It shows that when the coagulating time is 1.18×10^{-9} second, the particle size (r_s) is concentrated on 2 nm, and located at the lower limit comparing with the experiment data — 2–4 nm. Here the distribution finction of the coagulating particles is logarithm. The distribution plot by the calculation is shown in dot line in the Fig. 3. The above results illustrate that it is enough for the UFD to be coagulated in reaction zone (less than 10^{-9} second).

3) The 'melt point–size' effect. The calculation about the coagulating is without any condition. Actually, when the particles become big enough, the melt point will go up. In the calculated pressure and temperature, the situation is already in solid state. Therefore, the particles can not be coagulated after colliding. When this limit condition is added to the process, the time that particles size is coagulated to 5 nm increased to 10^{-7} second range which is almost the same range as the detonation reaction time. It is deduced that the limitation of the particle size would come from the limitation of the coagulating process.

In reaction zone, the explosive decomposes continuously and the free carbon is produced corespondingly. Along with the growth, the carbon drop began to crystallize to solid. The following calculation will prove that the crystallizing process in this zone is very little.

2.3. The section of Tailor expansion. In this section, the decomposing of the explosive is completed. Although there are chemical reaction, the heat effective is no longer to support the leading shock wave. The Tailor wave will make the temperature and the pressure go down steeply. In this thermodynamic situation, the crystallizing process starts. If the state is located in the diamond stabilization zone the diamond will be turn out, and if the state is located in the graphite zone the crystallized diamond would be turned into graphite (called graphitization). At the same time, another kind solid carbon would be formed. As the temperature dropping, the graphitization process of the diamond will stop, and the diamond exists in metastable state — this is the UFD we want to get.

As the heat effective of the phase transition and the volume effect are very small relatively, the process can be divided into two steps. In the first step, the mechanics process and the chemical reaction process are considered and we can get rules of temperature, pressure, specific volume and the free carbon quantity along with time. In the second step, the crystal dynamics process is considered on the basis of conditions gained in the first step.

2.4. The calculation on the crystal dynamics of UFD forming. In the detonation, the crystallizing process of the liquid carbon is carried out under the supercooling condition, and it can be described by using the spontaneous crystallization theory according to the process of crystal nucleus's nucleation and growth.

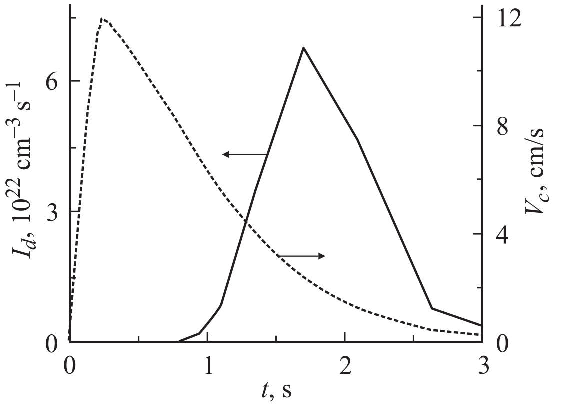

Figure 4. The nucleation rate and the growing velocity of UFD.

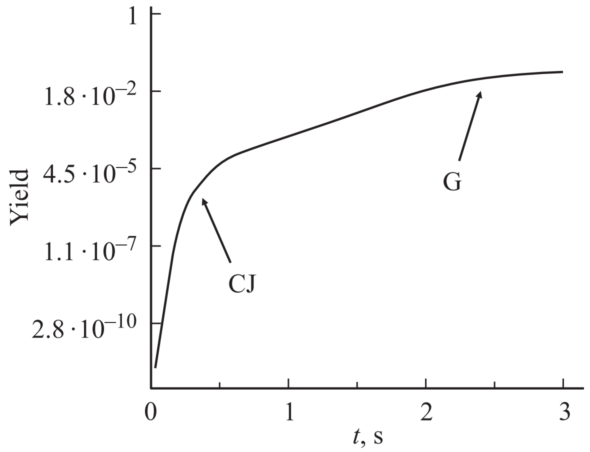

Figure 5. The yield of UFD. CJ — the end of chemical reaction zone and the beginning of Taylor zone; G — the graphitization point.

From the Von Neumann peak to the Tailor expansion zone, a special computing programm was worked out. The yield (out from per explosive mass) of UFD was calculated. The relations of $I_d(t)$, $V_c(t)$ and $Y_{ie}(t)$ are shown in Fig. 4. and 5 (where I_d — nucleation rate of diamond, V_c — growing velocity of UFD, and Y_{ie} — yield of UFD). It can be seen from the Fig. 5 that the yield of UFD is only 1.1×10^{-6} till the CJ point. This means that the UFD was formed mainly in the Tailor expansion zone.

3. The synthesis and purification technology of UFD

3.1. Detonation synthesis. The raw materials of the synthesis of UFD in our research is a kind of mixed explosive — TNT/RDX. The detonation of the explosive provide not only the carbon resource, but also the high pressure and high temperature conditions needed for forming UFD, which makes the synthesizing method relative simple. In order to gather the detonation products — detonation soot, and to fill the protection media, a pressurized metal vessel as the explosion tank was used in the experiment. It is clear that the partial of the explosives, the kind of the protection media and the charge structure are key factors to determine the synthesis rate of UFD.

3.2. Chemical purification. The purification technology plays a very important role in the production of UFD, which contributes the main part to the production cost and affects the products quality in a certain extent. By means of XRD, TES and laser Raman spectroscopy, it was found that the main impurity of the detonation soot is nanometric graphite and amorphous carbon, which can be cleaned away by the oxidation technology. The normal pressure perchloric acid technology (as perchloric acid technology), the high-pressure dilute nitric acid technology (as nitric acid technology) and the using permanganate kalium and sulfuric acid technology (as permanganate kalium technology) are three of the practical methods in our study.

The perchloric acid technology is used earlier. It has advantages of simple equipment and good purification efficiency, but has disadvantages that chlorine gas and other harmful gases as well as waste acid are produced in the reaction process, which can result in serious environment pollution. It is limited in doing experiment. The nitric acid technology from Russia is a relative advanced one with high automatic control level. However, at high pressure and high temperature situation, the dilute nitric acid needs expensive titanium as the reaction vessel to keep out of the corrosion, thus a big investment is inevitable for the use of this technology. Even though a medium production line with yield of UFD 10^7 carat/year has been set up already in the experiment area of our university. Comparing the above two technologies the permanganate kalium technology can make up some shortages of them. It has properties of efficient, economical, safe and less environment pollution, and is easy to be put into commercial use. The most important is that the method can get better purification result than others

Table 1. Purifying results of UFD by different technologies (from XPS)

Purification technology	Perchloric acid	Nitric acid	Permanganate kalium
C (diamond) %	89–92	86–92	90–94

Table 2. Further purifying results of UFD (from XRF)

Element Content, %	C 98.591	Fe 0.303	Cr 0.219	Ti 0.200	Ba 0.042
Element Content, %	Cl 0.025	S 0.025	P 0.001	Si 0.021	Al 0.032
Element Content, %	Cu 0.316	Ca 0.025	K 0.030	Mg 0.042	Na 0.128

Table 3. Particle size distribution of UFD purified by different technologies (from SAXS)

Technology	Perchloric Acid			Nitric Acid			Permanganate Kalium		
Size Interval, nm	$f(D)$, % nm	Mass Fraction, %	Cumulative, %	$f(D)$, % nm	Mass Fraction, %	Cumulative, %	$f(D)$, % nm	Mass Fraction, %	Cumulative, %
1–5	100	34.9	34.9	66.2	23.9	23.9	79.2	27.1	27.1
5–10	95.1	41.4	76.3	100	45.2	69.1	100	42.8	69.9
10–18	23.1	16.1	92.4	28.6	20.6	89.8	30.3	20.8	90.7
18–36	2.2	3.5	95.9	4.3	6.9	96.7	1.8	2.8	93.6
36–60	2.0	4.1	100	1.5	3.3	100	3.1	6.4	100
Median Size D_{50}, nm	9.3			10.5			10.8		

discussed above. At present, this technology is suitably applied in 10^5 carat / year scale production.

The purifying results of UFD tested by means of XPS are listed in the table 1, from which the purity of UFD that got from the permanganate kalium technology is superior to that from the perchloric acid technology and the nitric acid technology. If make further treatment, the purity of the products can be improved even better. Here is an example in table 2, which data comes from XRF.

Furthermore, some differences are in existence among the particle sizes of UFD purified through different technologies. Table 3 shows the test results by SAXS. It can be found, of the three sets test of data, that the particle size distribution from nitric acid technology is closer to which from permanganate kalium technology.

4. Conclusion and Prospect

1) The synthesis mechanism of UFD was established by qualitative analysis and quantitative calculations including explosion thermodynamics, coagulating dynamics of carbon drop and phase transition. The results show that the calculation can be used to forecast the forming process and the yield of UFD.

2) The synthesis and purification technology of UFD were studied systematically. The characteristics of three purification technologies were discussed, which are suitable for different scale production.

3) It is believed that UFD that possesses some of the properties both diamond and nanometer particles will has a bright future.

References

[1] S.R. Yun, F.L. Huang, F. Ma, Y. Tong, P.W. Chen, G. Zhou, Q. Chen, S. Zhao. Study and Development World Sci. Technol. **22**, *1*, 39 (2000).

[2] A.M. Staver, A.I. Lyamkin, N.A. Gubarev, E.A. Petrov. Fizika Goreniia i Vzryva. **20**, *5*, 100 (1984).

[3] K. Yamada, A.B. Sawaoka. Carbon **32**, *4*, 665 (1994).

[4] K. Liffman. J. Computational Phys. **100**, 116 (1992).