

Lee Davison Yasuyuki Horie
Toshimori Sekine
Editors

High-Pressure Shock Compression of Solids V

Shock Chemistry with
Applications to
Meteorite Impacts



Springer

The shock waves produced by meteorite impacts give rise not only to the obvious craters seen on planets and their satellites but also to subtle effects seen only with chemical and petrographic examination of the shocked material. Shock waves in the interplanetary and interstellar medium play an important role in the formation of stars and planets, including the Solar System. They also produce important chemical effects in interstellar clouds of dust and gas—including the production of rather complex organic molecules.

This volume is concerned primarily with the chemical and physical effects of shock waves on typical Earth and planetary solid materials. The emphasis is on comparing naturally occurring materials with similar materials produced by shock compression in the laboratory. Such comparisons can provide clues about the environment and events that produced the natural materials.

The chapters in the book deal with three main topics:

- methods used to investigate the effects of shock on recovered minerals and rocks
- effects of shock on carbon and hydrocarbons
- subtle effects of shocks on geochemistry, such as shock-induced redistribution of lead isotopes, the effect of the great impact at the end of the Cretaceous on atmospheric SO₂ and CO₂, and the effect of shocks on ices.

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With 94 Illustrations



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Shock Wave Chemistry and Ultrafine Diamond from Explosives in China

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6.1. Introduction

For a long time chemists have been trying to find new routes to stimulate chemical reactions. The shock wave is a special form of energy delivery that can produce very short pulses of high pressure and high temperature in materials. Using the energy of shock waves produced by explosive detonation to initiate chemical reactions is one of the new applications of explosives. Induction of chemical reactions by shock waves is an unique method in chemical research, which, unfortunately, is not very well studied. Relatively few types of shock-induced chemical reactions have been investigated and their reaction mechanisms are scarcely studied. Synthesis of ultrafine diamond from explosive detonation can be included in shock-wave chemistry, because explosives used as raw material are first decomposed by a strong shock wave to form free carbon atoms or clusters, which are then transformed to diamond under the action of high pressure and high temperature. In this chapter the research work in these fields carried out in China during the past decade is reviewed briefly, and some general suggestions to accelerate research work in these fields are given.

6.2. Shock-Wave Chemistry

Most of the subjects of studies on shock-wave chemistry are solids. It is well known that under the action of shock waves, solids experience strong mechanical effects, such as strong shearing, intense friction, high-speed motion, mutual mixing, etc. Under these actions many chemical reactions (chemical activation, phase transformation, decomposition, combination, etc.) can be induced. In the early 1980s Chinese scientists started research work in this field, including the synthesis of diamond from graphite, synthesis of barium titanate from oxides, and crystallization of an amorphous iron–nickel–phosphorus–boron alloy. All of these activities were reviewed by Jing [1]. At the beginning of the 1990s, some new research work in these fields was started.

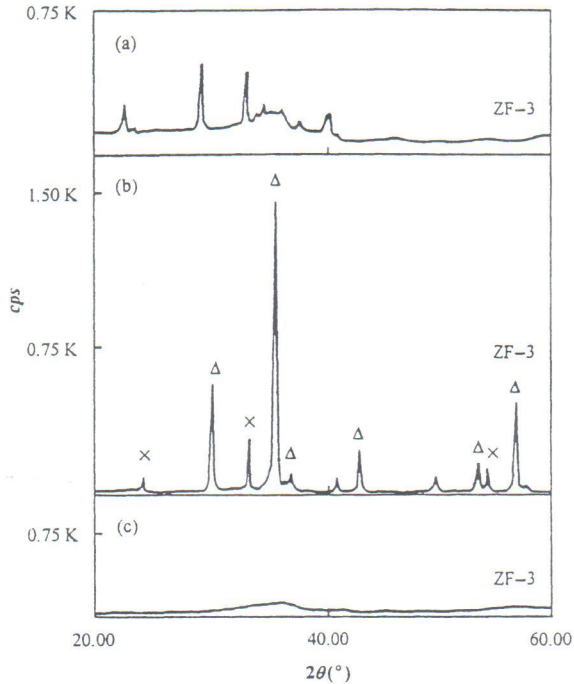


Figure 6.1. XRD patterns obtained from (a) a co-precipitated mixture of ZnO and Fe₂O₃, (b) zinc ferrites synthesized by calcination and (c) by shock wave treatment.

6.2.1. Shock Wave Synthesis of Nanosized Composite Metal Oxides

Xu et al. [2] carried out systematic research on the preparation of ferrites by shock waves. The starting materials are prepared by the co-precipitation of zinc nitrate or nickel nitrate solutions by ammonium hydroxide. As confirmed by XRD (X-ray diffraction) patterns (see Fig. 6.1a), the co-precipitated mixtures are made of nanosized particles of zinc oxide or nickel oxide with ferric oxide. Shock-wave treatments were performed using the impact of steel plates driven by a light gas gun or by explosive detonation. Hugoniot data for zinc oxide and ferric oxide were measured on the light gas gun, separately, and were used to calculate the shock parameters in the samples. The products obtained after shock treatment were investigated using XRD, TEM (transmission electron microscopy), electron diffraction, and SAXS (small-angle X-ray scattering) methods. From the XRD patterns (see Fig. 6.1b) it can be seen that the products of shock-wave treatment, in contrast to the zinc ferrite synthesized by high-temperature calcination, are XRD amorphous, that is, no diffraction peaks appeared in their XRD patterns. Electron dif-

fraction of the shock-treated product gave only diffraction rings, with the distances between them confirming that the product is zinc ferrite or nickel ferrite. The crystallites produced are so small (2–3 nm) that they generate neither XRD diffraction peaks nor electron diffraction spots. From the TEM micrographs and the results of SAXS it is found that, although the crystallites of the shock-wave-synthesized zinc or nickel ferrites are very small, the particle sizes of these products are rather large, that is, a large number of crystallites agglomerated into one particle.

The magnetic properties of ferrites synthesized by shock-wave treatment were measured and compared with those of product synthesized by calcination. The saturated magnetization of nickel ferrites prepared by different methods are shown in Fig. 6.2. It can be seen that the products synthesized by shock waves have much higher saturated magnetization than that of the products synthesized by calcination. There exists an optimum shock pressure giving the highest magnetization; higher shock pressures cause a lowering of magnetization. A possible reason for the high saturated magnetization is that, under shock treatment, a nonstoichiometric product is formed, in which the distribution of cations in sublattices is different from that formed in calcination. This is a new phenomenon and more research is needed to elucidate it in detail.

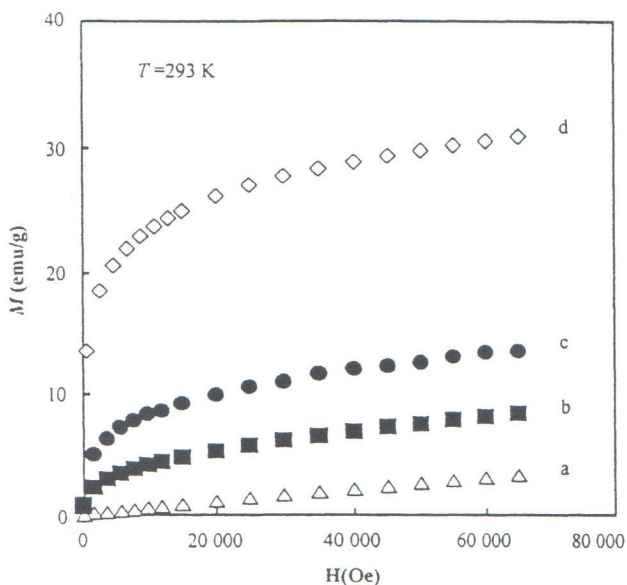


Figure 6.2. Curves of magnetization for shock synthesized nickel ferrites and the precursor material. (a) Co-precipitated mixture of nickel oxide and ferric oxide; (b) nickel ferrite synthesized by calcination; (c,d) nickel ferrite synthesized by shock waves of 27.6 GPa and 23.4 GPa, respectively.

Zinc ferrite is a good photocatalyst, which can catalyze a number of photochemical reactions under the action of light. The photocatalytic activities of zinc ferrite synthesized by two methods were measured in the reactions of dehydrogenation of H_2S and methanol. In both reactions hydrogen is one of the main products, so the rates of hydrogen formation are a measure of the photoactivity of the catalysts. Experimental results (see Fig. 6.3) show that the photocatalytic activities of the shock-wave-synthesized zinc ferrites are much higher than those of the calcination synthesized ones, and the photocatalytic activities increase with an increase of shock-wave pressure. The possible reasons for high photocatalytic activities of shock-wave-synthesized samples are the small sizes of particles and the higher densities of defects formed by shock-wave treatment.

These results demonstrate that shock-wave synthesis is a novel method to prepare nanosized materials with some unique physical and chemical properties. In the light of the experimental results, nanosized zinc ferrite and nickel ferrite synthesized by shock-wave treatment may have potential applications as magnetic materials and photocatalysts.

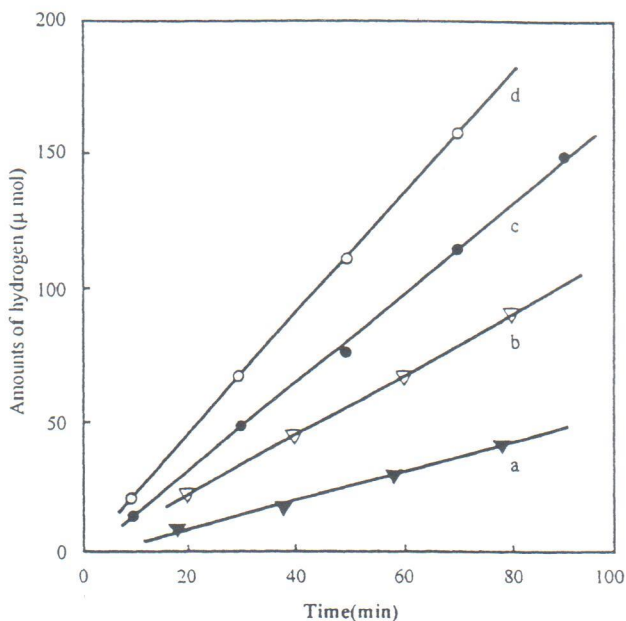


Figure 6.3. Photocatalytic activities of zinc ferrites synthesized by different methods: (a) by calcination; (b,c,d) by shock wave treatment with initial pressures of 8 GPa, 20 GPa and 37 GPa, respectively.

6.2.2. Shock Wave Activation and Modification of Inorganic Solids

Under the action of a strong shock wave large numbers of defects are formed in solids, causing significant changes in their structure and properties.

Because the catalysts widely used in petroleum and chemical industries are inorganic solids, the activation and modification of different kinds of solid catalysts by shock waves were investigated by Xu and colleagues [3,4].

Magnesium oxide (MgO) is an important component in many industrial catalysts. Xu et al. [3] carried out a series of studies on the activation and modification of conventional powdered and crystallized MgO under the action of shock waves. After shock-wave treatment, the recovered samples were characterized by XRD, TEM, ESR (electron spin resonance), FT-IR, and CO₂-TPD (temperature programmed desorption). Figure 6.4 shows the changes of the ESR signals of crystalline MgO. It can be seen that some new signals appear, which may be caused by the formation of defects due to shock-wave treatment. The changes in catalytic performance after shock-wave treatment were studied in the catalytic dehydrogenation and isomerization of butene, oxidative dehydrogenation of ethane, and catalytic dehydrogenation of propane, which, to our knowledge, is the first systematic research of this kind. The main results obtained are as follows: XRD and TEM results indicate that the density of defects and distortion increased remarkably. Results of ESR show a significant increase of defects after shock-wave treatment. Results of catalytic performance measurement show that, for all reactions studied, the conversions of raw materials and the selectivities for products sought increase after shock-wave treatment. The results of CO₂-TPD show that the temperatures of desorption peaks for MgO before and after shock-wave treatment are nearly the same, but the area of the desorption peaks increased significantly. These results show that the strength of the basic sites on MgO remains almost unchanged, but the concentration of basic centers increases greatly. Perhaps, this is the main reason for the improvement of the catalytic performance of MgO after shock-wave treatment.

Titanium dioxide (TiO₂, anatase) is an important photocatalyst. Xu et al. [4] investigated the photocatalytic activities of TiO₂ after shock-wave treatment. They observed that the photocatalytic activities of anatase in the reactions of dehydrogenation of H₂S and methanol are enhanced by a factor of 2–3 after shock-wave treatment. It is believed that the increase of photocatalytic activity is related to the increase of residual strains and dislocation defects due to shock loading, which is confirmed by the analyses of XRD and UV-vis diffuse reflection spectroscopy. The large density of defects in turn reduces the energy gap of TiO₂, which, perhaps, is the main reason for the enhancement of its photocatalytic activity.

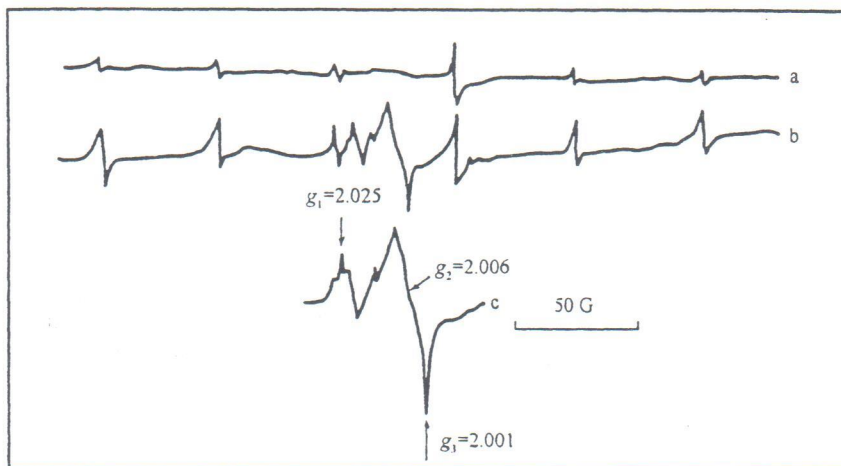


Figure 6.4. ESR spectra of crystalline MgO: (a) Original MgO; (b) after shock wave treatment; (c) enlarged signals of (b).

Aluminum nitride (AlN) is a ceramic material. Improvement of the sintering characteristics of AlN by shock-wave activation was investigated by Xue et al. [5]. The activation of AlN was carried out by shock waves with a pressure of 9.8 GPa. After treatment, the dislocation density increased to 10^{11} cm^{-2} and the strain to 2.85×10^{-3} . These values are much higher than those in the original sample. Sintering of the shocked sample at 1640°C gives a compacted product with a density up to 98 % of the theoretical density, whereas the unshocked sample gives only 80 % of the theoretical density after sintering under the same conditions [5]. $\text{Sm}_2\text{Fe}_{17}$ alloy is an excellent magnetic material. Gao et al. treated it with a shock wave of 1.4–4.0 GPa and obtained a sample that absorbed a much larger amount of nitrogen to form $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ with higher stability, higher Curie temperature and improved magnetic property relative to the original material [6].

All these results imply that it is possible to activate solids by shock waves to prepare solid materials with improved physical and chemical properties. However, the mechanisms of activation and improvement of the material properties are still not very clear, and more detailed investigations are required.

6.2.3. Shock-Wave-Induced Phase Transitions

Many solid substances exist in several crystalline forms, in which the arrangement of atoms or molecules is different. Under the action of shock waves, atoms or molecules in solids undergo high-speed motion that results in their rearrangement, that is, a phase transition takes place. In China, as in many other

countries, the first important work in this field is the shock-wave-induced transition from graphite to diamond.

Phase Transition of Graphite to Diamond

Shao et al. started their work on phase transition of graphite to diamond in the 1980s and developed a new device for the synthesis of diamond from graphite by shock waves [7]. Two samples were used: a cylindrical one was subjected to the action of sliding detonation of explosives, which converted 8–10 % of the graphite to diamond. The detonation of this charge also accelerated a steel plate to impact on the second sample, in which the graphite is further converted to diamond. With this device using 1 kg of TNT explosive they obtained 7–8 g of diamond. Based on this result, they carried out the diamond synthesis in blasting work. In a typical blast, 600 kg of explosives and 10.5 kg of sample (graphite–iron powder = 30:70) were used and 3.5 % of the graphite was converted to diamond. Chen et al. [8] investigated the phase transition of pure graphite to diamond without adding any catalysts or cooling agents. Using multiple shock compressions, polycrystalline cubic diamond was obtained. The highest graphite conversion was 8.2%. Wu et al. treated gray cast iron by shock waves and found cubic and hexagonal crystalline diamonds in the product, the texture structure of which was also studied [9].

Phase Transition of Boron Nitride

Boron nitride is an important superhard material. Preparation of superhard w-BN and c-BN by phase transition of g-BN induced by shock waves has been a hot research topic in the last decade. In China, early work in this field was done by Yun and colleagues [10]. Using an annular detonation wave generator to produce sliding detonation, about 20 % of g-BN in a steel tube could be converted to w-BN.

Tan et al. carried out a more systematic investigation in this field [11]. Using inward sliding detonation and a cylindrical sample tube, they converted g-BN to w-BN and found that the G.I. (graphite index) of the green material had a great influence on the conversion of g-BN to w-BN. The highest conversion is 95% for the starting g-BN powders of G.I. value of 1.18. The content of impurities in the chemically purified w-BN products is less than 0.5%. Figure 6.5 shows the typical morphology of shock-synthesized w-BN. The gray superhard ceramic powder has a particle size ranging from submicron to a few microns and a BET specific surface area of 29 m²/g. Each particle consists of a large number of small crystallites of about 17.5 nm in size according to the Scherrer formula. It is also found that there is a rather high defect concentration (mainly N-vacancies) in the product, so the specific volume of the product (3.26 m³/g) is higher than that of perfect crystalline w-BN (3.454 m³/g). The thermal stability of w-BN synthesized by shock waves is fairly good. The starting temperature of



Figure 6.5. TEM micrograph of shock synthesized w-BN (4000 \times)

exothermal reaction in air is 780 °C, which is lower than that of cubic BN (c-BN) (1000 °C), but significantly higher than that of micro-diamond powders (600 °C). An exothermic reaction peak appearing at about 1120 °C in Ar signifies the occurrence of the reverse transition from w-BN to g-BN. In their work Tan et al. also discussed the transition mechanism of g-BN to w-BN.

The phase transition of BN was also investigated by Li et al. [12]. Fine particles of h-BN with G.I. of 7 and purity higher than 98 % as the raw material were treated by shock waves with a pressure of 70–90 GPa produced by high-speed impact of a steel plate. The product obtained was w-BN, with a small amount of c-BN. A “chair model” was suggested for the mechanism of this phase transition, in which g-BN can be converted directly to c-BN without formation of w-BN as an intermediate. They suggested that the yield of c-BN can be increased significantly by increasing the pressure and duration of the shock wave.

Phase Transition of Other Materials

There are many works dealing with the phase transition of other solids.

He and colleagues [13] treated a mixture of fullerene and nickel powder by shock waves produced by high-speed impact of a steel plate. They found that below 11.3 GPa no phase transition of C₆₀ occurs. Under shock waves with a

pressure of 33.7 GPa, C_{60} converts completely to diamond. They proposed that under the action of shock waves molecules of C_{60} are smashed to carbon atoms and transformed to diamond structure by a diffusion mechanism, so the conversion of C_{60} to diamond is much higher than that of graphite.

Tang et al. [14] started their investigation on the phase transition of CdS and InSb under shock waves in 1993. In 1997, using more sophisticated instruments, they measured stress–time profiles at the impact surface and after transmission through 1–2-mm-thick CdS single crystals with higher time resolution. In their experiments, two-wave structures were found. Based on the experimental data they concluded that the CdS phase transition from wurtzite to rock salt phase is completed within 0.2 μ s under shock loading between 1.8 and 7.8 GPa, and the phase transition is a two-step process with an extremely fast first step (within less than 10 ns) and a rather slow second step of 0.1–0.2 μ s duration. The transition occurs directly from the elastic state prior to any plastic deformation. The transition stress is measured to be 3.25 ± 0.1 GPa, whereas the calculated average stress of phase transition is 2.29 GPa, which is in accordance with the static phase transition pressure (2.3 GPa). It is found that the shear stress has no effect on phase transition pressure. The authors also carried out a preliminary study on the phase transition of InSb single crystal under shock waves [15]. They found many differences between the behaviors of CdS and InSb. The most distinct feature is that shear stress, in contrast to the case of CdS, has a great effect on the phase transition of InSb single crystals.

As is known, the determinative factors of phase transition of solids are the pressure and temperature produced by shock waves, which, in turn, are determined by the strength of the shock wave and the properties of the solid; among them, the porosity of the solid is the most important factor. In samples of the identical material with different porosities, the sample with higher porosity results in lower pressure and higher shock temperature due to the adiabatic compression of gases included in the solid sample. On the contrary, lower porosity results in higher pressure and lower temperature. Xu et al. [16] carried out some preliminary experiments to confirm the different results in this respect. Titanium dioxide (anatase) was used as the starting material. The samples were prepared by compaction of anatase powders that were unfilled or were filled with liquid paraffin. Comparison of the material recovered after shock-wave treatment showed that, in the former case, rutile is the main product, that is, phase transition was caused mainly by the high shock temperature (nearly 470 °C when the shock pressure is 36.3 GPa), whereas, for the sample filled with liquid paraffin, the high-pressure phase of β - TiO_2 is the main product, which shows that, in this case, high pressure (about 46.8 GPa) plays the dominant role for the phase transition of anatase, and the temperature produced by shock wave is much lower (only about 2000 °C) than in the former case and plays only a minor role.

6.2.4. Other Shock-Induced Reactions

Shock waves can induce many chemical reactions of different types. Two rather important examples that have been investigated systematically in the past decade in China are changes of minerals and reactions between carbon (diamond or graphite) and water under the conditions of high pressure and temperature produced by strong shock waves.

Chemical reactions of minerals under high pressure are important in geological research. Shock waves can subject mantle materials to high pressures that are difficult or impossible to attain by static methods, so they are very useful for the study of the behavior of minerals in the earth's crust and mantle. Hydrous minerals may play a critical role in water storage in the earth's interior. They affect lower crust and mantle rheology, partial melting, and subduction behavior and hence aspects of the earth's evolution such as the regulation of the water budget and triggering of deep focus earthquakes. Accordingly, the study of hydrous minerals at high pressure and temperature is crucial for understanding the structure, physical properties, and evolution of the earth's crust and mantle. Gong et al. carried out a series of investigations in this field [17]. Crystalline halloysite (a kind of hydrous kaolinite) is an important mineral in deeply subducted Al-rich pelitic sediments. Samples of halloysite with two different initial densities were subjected to shock waves in the pressure range up to 100 GPa. Hugoniot EOS experiments were conducted on these samples. Both of the samples show changes in slope in shock wave velocity–particle velocity plane. Three distinct regions appear along both the Hugoniot. For the sample with initial density of 2.001 g/cm³, a low-pressure phase (LPP) exists for shock pressures up to about 35.8 GPa, a mixed phase region (MP) begins at 35.8 GPa and extends to about 44.4 GPa, and then a high-pressure phase (HPP) occurs at shock pressure between 44.4 and 100 GPa. For the sample with initial density of 1.375 g/cm³, the pressure ranges of its LPP, MP, and HPP cover 0–12.7 GPa, 12.7–22.9 GPa, and 22.9–50 GPa, respectively. Based on the Hugoniot of the possible intermediate compounds, it is inferred that the transformation process of halloysite with increasing pressure and temperature occurs via an intermediate decomposition phase of the assemblage [γ -Al₂O₃ + SiO₂ (stishovite) + H₂O] to the end phase [Al₆Si₂O₁₃ (mullite) + SiO₂ (stishovite) + H₂O]. This intermediate phase transition is, essentially, the result of dehydration. This result is also confirmed by shock recovery examination, in which the recovered samples were characterized using IR spectroscopy, XRD, and TEM techniques. Thermodynamic calculations were also carried out. Based on the above-mentioned results, the processes of phase transition and dehydration of halloysite were analyzed in detail, and an approximate phase diagram of halloysite in the range of up to 40 GPa and 2000 K is given. Recently, continuing the research in this field, the authors carried out similar investigations on other minerals, such as melanterite [18].

The reactions between carbon and water are important for understanding the nature of explosive detonation. Hu et al. [19] carried out a systematic research program on the chemical reactions between carbon (graphite or diamond) and water under the action of shock waves. The processes were examined by multi-channel emission spectroscopy. They found that behavior of the graphite–water mixture is different from that of the diamond–water mixture under shock loading to pressures below 19 GPa. As the shock pressure is increased beyond 23 GPa, the two shock Hugoniot become similar, which indicates that more graphite has been converted to diamond. When the pressure is raised to 52.9 GPa, the volume expands due to the formation of gaseous products from the reaction between carbon and water. Emission bands of C_2 , CO, and CO_2 appear when shock pressure is higher than 34 GPa, which indicates that chemical reactions between carbon and water begin at that pressure [18].

6.2.5. Numerical Simulation Methods in Shock-Wave Chemistry

In shock-wave-chemistry research, compacts of solid powders are usually used as samples. Because of porosity, the samples are inhomogeneous and not a continuous medium, so models based on continuum physics are not suitable for the numerical simulation of these problems. A discrete meso-dynamic method (denoted as DM^2) developed by Tang et al. in recent years is a better method for this purpose [20].

This model is based on quasimolecular dynamics, in which the medium is assumed to be composed of an assembly of meso-scale discrete particles (i.e., finite elements). The movement and deformation of the material system and its evolution are described by the aggregate movements of these elements. Two types of basic characteristics, geometrical and physical, are considered. In the geometrical aspect, shapes and sizes of elements and the manner of their initial aggregation and arrangement are the important factors. In the physical aspect, mechanical, physical, and chemical characteristics, such as the interaction potential, phase transition, and chemical reactivity may be the important ones. To construct this model, many physical factors, including interaction potential, friction of particles, shear resistance force, energy dissipation and temperature increase, stress and strain at the meso- and macro-levels, phase transition, and chemical reaction are considered. In fact, simulation of chemical reactions is one of the most difficult tasks, but it is the most important aspect in shock-wave chemistry.

Preliminary analyses were carried out by the authors, and a tentative DM^2 method was developed. Using this tentative method some practical examples were investigated, among them the shock-induced reaction of Al + Ni fine powder mixture and the stress profile of HMX explosive powders under the action of shock waves. The calculated results using this model are in better agreement

with the experimental results than those obtained by using the model based on continuum physics.

To make further improvement, Tang's group is now working on the development of a 3D DM² method, in which the pore collapse process is considered. At the same time, a new "region method" is suggested to replace the previous "window method" to reduce requirements for CPU time and RAM. [21].

6.3. Ultrafine Diamond from Explosive Detonation

There are several methods for artificial synthesis of diamond, among them preparation of ultrafine diamond powders from detonation of carbon-rich explosives is a fairly new method; the first published paper appeared in 1988. During the last decade research work in this respect was carried out in many countries. It is now generally believed that the first step of this process is the breakdown of C-C, C-N, C-O, and C-H bonds in the explosive molecules due to the high pressure and high temperature of the detonation. This forms carbon atoms, ions, or atomic groups, which then convert to diamond. Accordingly, this process is essentially a shock-wave-induced chemical reaction, and the formation of diamond in an explosive detonation can be considered as a special example of shock-wave chemistry. The most important feature of this kind of diamond is its nanosized crystallites, that is, the fundamental diamond crystallites formed in explosive detonation are tiny spheroids with diameter of about 5 nm. Different terms have been used by different authors to name this new kind of diamond, such as ultrafine diamond, nanostructured diamond, ultradispersed diamond, etc. In this review, the term *ultrafine diamond* is used. In China, research work in this field was started at the beginning of 1990s.

6.3.1. Preparation

In the first papers published in 1988, the detonation of explosives was carried out in inert gases, such as CO₂ and nitrogen, used as the protective atmosphere and cooling agent. The yield was rather low and the production method was rather complex and not suitable for mass production. Since then, much attention has been paid to improvement of the preparation method.

Based on the consideration that fast cooling of detonation products can reduce the graphitization of diamond, Xu et al. [22] suggested to use water as the cooling agent due to its high heat capacity. Two methods were developed: a water-jacket method and an underwater method. It is known that, when gaseous cooling agents are used, the solid product produced in one detonation must be removed before a subsequent detonation, because the shock waves produced by the subsequent detonation will produce high temperature in the solid products of the previous detonation and reduce the content of diamond in it. Unlike this situation, subsequent underwater detonations will not result in high temperature

in the solid products since the product is dispersed in water. Underwater detonation can be repeated many times in one portion of water without any effect on the diamond products. Thus, an underwater multiple detonation method is developed, which gives nearly the same yield of ultrafine diamond as in the single-detonation method (around 8%), and remarkably simplifies the production technology and increases the production efficiency.

Yun and colleagues investigated the effects of different cooling agents on the yields and properties of ultrafine diamond [23]. Water, ice, pyrolytic salt, and nitrogen gas were used as the cooling agents, and water is considered the best, giving the highest yield of diamond (9.1%). In other research, they investigated the effect of a Mach stem (in which the pressure of detonation products is three times the C–J pressure.) on the yield of diamond. When the pyrolytic salt is used as the cooling agent, the effect of the Mach stem is especially dominant, and raises the diamond yield to 12.5%.

Z.R. Hu of the Chinese Academy of Engineering Physics had done some research work in the synthesis of ultrafine diamond.

6.3.2. Inquiry Into the Mechanism of Diamond Formation

Much attention has been paid to the mechanism of formation of nanosized diamond in explosive detonations. Yun et al. carried out a systematic investigation of this problem [24]. They found that in the calculation of detonation parameters of explosives, such as detonation velocity or detonation pressure, if the liquid-like carbon is assumed to be present in the detonation products and its equation of state is used, the calculated results are in better agreement with the experimental data. Thus, it is assumed that, in detonation of carbon-rich explosives, excess carbon converts to carbon atoms, ions, or clusters composed of a few carbon atoms, which condense into liquid carbon micro drops during collisions. In the expansion and cooling of the detonation products, the tiny liquid carbon droplets convert into tiny diamond crystallites. To answer the question why the liquid carbon droplets do not grow to larger ones, the authors, using the theory of homogeneous nucleation and growth of crystallites, estimated the sizes of diamond crystallites formed under the thermodynamic conditions of detonation and obtained results that are in fairly good agreement with the experimental observations [25]. On the other hand, using the quick coagulation theory of colloids, the authors estimated the degree of growth of carbon micro droplets during the period of detonation (10^{-7} s). Again their calculated results are in agreement with experimental results [26].

It is clear that all these results give only indirect evidence for the mechanism of diamond formation in detonation of explosives. In order to confirm the hypotheses suggested above, experimental evidence is necessary. Because of the complexity of detonation products, the very short duration of the detonation process, and the very high pressure and temperature in the detonation zone of

explosives, it is very difficult to get experimental evidence for the mechanism of the formation of UDD during the detonation process. Hence, very little progress has been made in this respect up to now.

6.3.3. Properties

The ultrafine diamond obtained by explosive detonation possesses two distinguishing features: nano-scaled particle sizes and surface functional groups.

The XRD pattern of ultrafine diamond shows the characteristic peaks of cubic diamond, but no peaks of hexagonal diamond, which confirms that the product obtained by the explosive detonation is pure cubic diamond without hexagonal diamond. This is confirmation that, in detonation products, the ultrafine diamond is formed directly from carbon atoms or atomic clusters, and not from the phase transition of graphite. The absence of a diffraction peak of graphite in the XRD pattern indicates that the content of graphite in ultrafine diamond is less than 5%, but there is some protrusion in the range of 20 degrees, which indicates the presence of a certain amount of amorphous carbon. For this reason, it is believed that the purity of ultrafine diamond prepared by explosive detonation is not less than 95%. Using the XRD technique, Yun et al. [27] measured the crystallite size and micro stress of ultrafine diamond obtained by different cooling agents. It is confirmed that using water as the cooling agent the crystallite sizes are 4–6 nm, which is in agreement with the results of the TEM observation. It is also shown that the micro stress of ultrafine diamond is much higher (about 2–10 times) than that of diamond synthesized by static high pressure [26]. The crystallite sizes were also be calculated from the Raman spectra of ultrafine diamond. The width and the shift of the Raman 1332 cm^{-1} characteristic band gives crystallite sizes of diamond, which are in agreement with the results obtained by XRD.

Xu et al. [29] obtained some high-quality TEM and HREM (high-resolution electron microscopy) microimages of ultrafine diamond, which directly confirmed that the crystallite sizes are of 5–10 nm (see Fig. 6.6a). In the HREM micrographs the crystalline lattice images can be seen and it is confirmed that each nano-scaled crystallite is a single crystal, but defects are often present in them (see Fig. 6.6b). From the TEM image it is also seen that the tiny diamond crystallites coagulate into micrometer-sized agglomerates with loose fractal structure (see Fig. 6.6a), which is also verified by their high specific surface area (about $300\text{--}400\text{ m}^2/\text{g}$).

It is interesting to mention that, after treating the solid detonation products with oxidative acid and followed by washings with water, a very stable slurry of diamond particles in water is obtained, which contains only 7–10 wt% of diamond. This slurry can remain stable for a long time, months, even years. Referring to the TEM images, it is proposed that the stable slurry is composed of

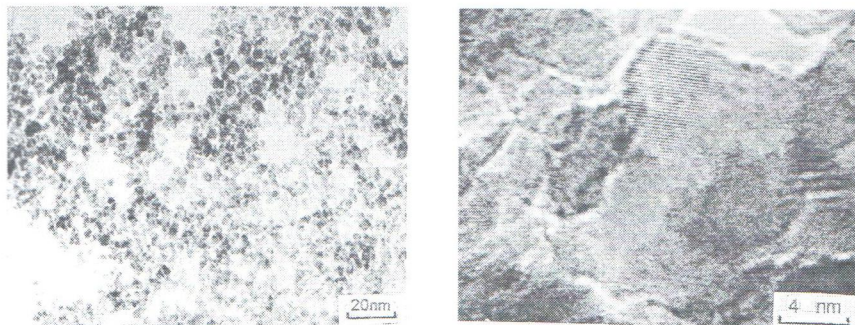


Figure 6.6. TEM(a) and HREM(b) microimages of ultrafine diamond from explosive detonation [29].

the 3D network of diamond crystallites with water filled in their hollow spaces. Further work is now in progress in our laboratory to unravel the nature of this stable slurry.

Many efforts were devoted to the de-agglomeration of the ultrafine diamond, but none has been successful in getting the mono-dispersed suspension. In most of the research done to obtain such a suspension, surface-active agents and ultrasonic treatment were used, but the minimum sizes obtained were no less than 300 nm. One of the difficulties is that the nature of agglomeration of nano-diamond crystallites is not clear. It is believed that chemical bindings may exist between agglomerated diamond crystallites, that is, “hard agglomeration” takes place between the diamond nano-crystallites to form agglomerates of fractal structure (see Fig. 6.6a). In this case, chemical treatment should be used for the de-agglomeration. We have tried many chemical methods for this purpose, but no effective method has been found. The solution of the problem of de-agglomeration is one of the key steps in developing new applications of ultrafine diamond. More attention should be paid to research work on this subject.

Jiang et al. [30] carried out detailed investigations of ultrafine diamond using FT-IR spectroscopy. The results clearly show that one of the distinguishing features of ultrafine diamond is the existence of surface functional groups. Detailed analysis of the spectra shows that many oxygen-containing and nitrogen-containing groups, such as hydroxyl, carbonyl, carboxyl, etheral, esteral, amide, and cyano groups exist on the surface of diamond. These results are in agreement with the results of elemental analysis and XPS. The results of elemental analysis indicate that the content of oxygen in ultrafine diamond reaches about 10%, which is a significant difference between the ultrafine diamond synthesized by explosive detonation and natural diamond or synthetic diamonds prepared by the high-static-pressure method. XPS analysis gives nearly the same content of oxygen, indicating that almost all the oxygen atoms exist in the form of oxygen-containing functional groups on the surface of diamond crystallites.

Ultrafine diamond treated with different gases, including hydrogen, nitrogen, methane, air, etc., at high temperature, were examined using FT-IR spectroscopy. After the treatment with hydrogen the intensity of C-H absorption bands increases, while most of the surface oxygen-containing groups remain. Treatment with nitrogen or methane also increases the intensity of the C-H bands, but here the main reactions are decarbonylation and decarboxylation, which convert the carbonyl and carboxyl groups to C-H groups. After heating in air above 400 °C the IR absorption band of C-H (ca. 2900 cm^{-1}) decreases in intensity, and the IR bands of oxygen-containing groups increase in both intensity and wavenumber, which denotes the oxidation of surface C-H bonds and the variation of the oxygen-containing species. Using *in situ* FT-IR technique, the adsorption of water on the surface of ultrafine diamond was investigated by Ji et al. [31]. It is found that ultrafine diamond adsorbs water very quickly, which is quite different from ordinary synthetic diamond. In the spectrum of a completely dried sample of ultrafine diamond, no water absorption band at about 3420 cm^{-1} is observed, but after exposing the sample to air for only a few minutes, a strong water absorption band appears (see Fig. 6.7). The existence and nature of surface functional groups on ultrafine diamond is worth studying in detail. Making full use of the nano-scaled particle sizes and the surface functional groups may open new applications for ultrafine diamond.

6.3.4. Applications

Application of ultrafine diamond is a special field and to discuss it in detail is beyond the scope of this chapter, so only a brief account is given.

Synthetic diamond obtained by static high pressure is widely used in many industries; these applications are called “traditional” applications. Xu and colleagues have carried out research work to use the ultrafine diamond instead of the diamond synthesized by static high pressure in some of these traditional applications. For example, by addition of ultrafine diamond to the solutions for electroplating or brush electroplating of nickel, steel can be given ultrahard and wear-resistant composite nickel coatings. The surface hardness of this material is nearly 50% higher and wear resistance several times larger than a pure nickel coating prepared under the same conditions [32]. The use of ultrafine diamond as a polishing agent in magnetic fluid polishing of ceramic balls also gives good results, the surface roughness can be reduced to 0.013 μm [33]. Addition of ultrafine diamond to lubricating oil can reduce frictional wear. It can be seen from Fig. 6.8 that addition of ultrafine diamond to paraffin oil in an amount of only 1% can reduce the worn volume significantly; and the worn volume increases only slightly with the increasing loadings. Under 200 N it is only a sixth that of pure paraffin oil [34].

The ultrafine diamond was also used as seed to prepare CVD diamond films. This led to a significant increase in the growth rate and the density of nucleation

in the CVD diamond film [35]. Jin et al. have tried the use of ultrafine diamond as seed in the static-high-pressure synthesis of diamond. Preliminary results show that the addition of ultrafine diamond can increase the transition of graphite to diamond, and can increase the percentage of coarse grains in the product.

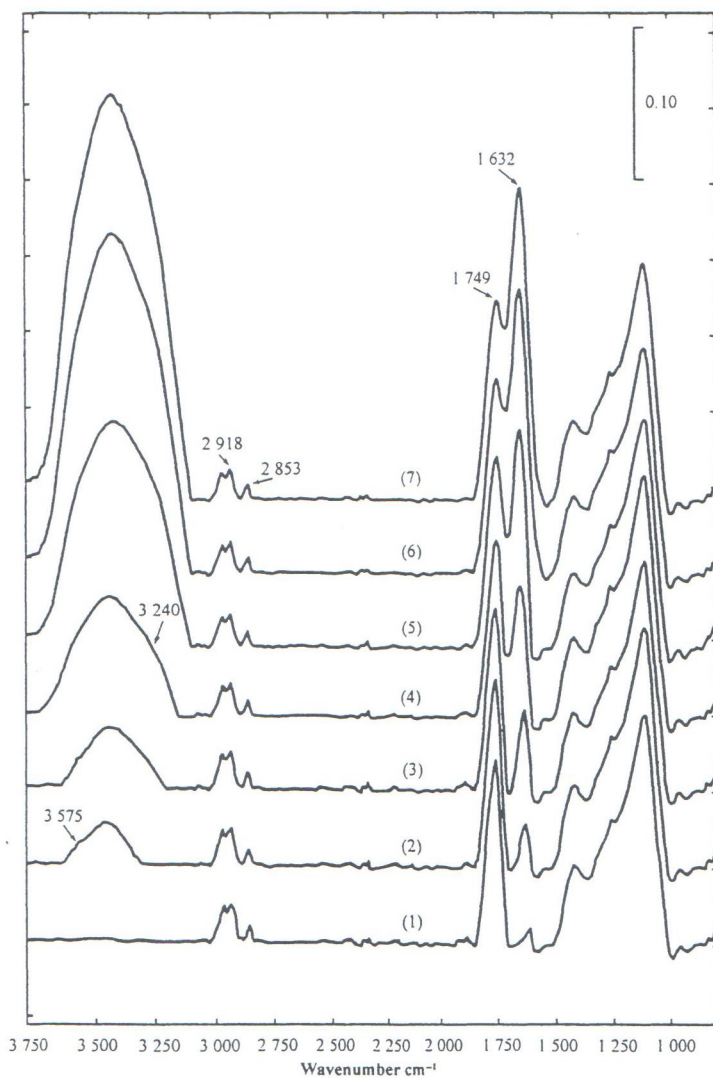


Figure 6.7. FTIR spectra of AgCl-ultrafine diamond pellets after exposure to air over different periods of time. (1) Heated in an *in situ* IR reactor cell at 140 °C for 4 h and then recorded *in vacuo*; (2) exposed in air for 2; (3) 10; (4) 30; (5) 60; (6) 90; (7) 140 min [31].

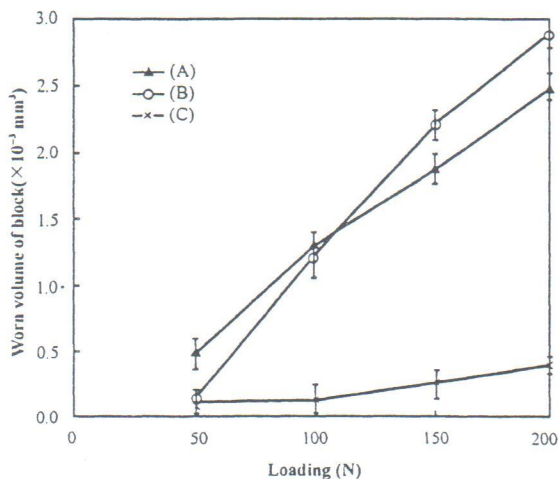


Figure 6.8. Variation of worn volumes with loading: (a) paraffin oil; (b) paraffin oil + 1% graphite powder, and (c) paraffin oil + 1% ultrafine powder from explosive detonation [34].

In the above-mentioned applications the use of ultrafine diamond to replace traditional diamond prepared by static pressure has some advantages, but they are not significant enough to attract the attention of industrialists, so commercial utilization has not been realized. In our opinion, the emphasis of application research should be put on nontraditional applications, that is, to make full use of the unique features of ultrafine diamond synthesized by explosive detonation: the nano-scaled crystallite sizes and the surface functional groups. In recent years, some research has been carried out in this aspect. Field electron emission of the ultrafine diamond film was investigated and fairly good results were obtained [37]. When ultrafine diamond is used as a filler in adhesives, their strength after solidification is nearly 50% higher than that of a sample without ultrafine diamond [38].

It is evident that creative work in this field is rather limited. We strongly believe that when more research work has been carried out, new important applications of the ultrafine diamond synthesized by explosive detonation could be developed.

6.3.5. Some Important Research Topics Concerning Ultrafine Diamond from Explosive Detonation

As mentioned above, although more than ten years have passed since publication of the first papers on ultrafine diamond synthesized by explosive detona-

tion, many problems remain to be solved. The following are some of them, along with some suggestions concerning future research.

Preparation

Increase in the yield of ultrafine diamond is the main goal of research in preparation. Addition of other carbonaceous compounds to the explosive charge to increase the content of free carbon in the detonation zone could be a good route to increase the diamond yield. Here, the first choice is to use compounds that are easily decomposed to carbon atoms or carbon ions in the detonation wave. In order to realize the ideal detonation and to reach the needed detonation pressure, charge diameters and content of high explosive (e.g., RDX) should be increased. Simpler and more effective methods of purifying diamond should be developed. The air oxidation method offers good potential for improvement, but more research work on designing a reactor suitable for large-scale production must be undertaken first. Investigation of routes to increase the efficiency of the oxidation process and to reduce the loss of diamond is also important. The use of certain suitable catalysts is a possible and hopeful way to achieve this goal.

Properties

It is commonly recognized that a comprehensive understanding of the properties of a new material is an essential prerequisite to finding its new applications. In this respect, the study of ultrafine diamond is incomplete and its properties remain to be fully elucidated. For example, the nature of the surface functional groups and the method of their modification; the nature of the agglomeration of ultrafine crystallites and effective methods of de-agglomeration to prepare mono-dispersed suspension; the crystalline and surface structures of the nano-scaled diamond, etc., are appropriate subjects of research. An efficient method for the determination of particle size distributions and structures of nano-sized particles in suspension is very important, and is worth developing in the near future.

Applications

Among the traditional applications, using ultrafine diamond to get better results in ultrafine polishing, thin wear-resistant coatings, additives for lubricants, etc., is possible. More development work should be done to realize the practical applications of these techniques in production. Nevertheless, the emphasis of development work should be put on nontraditional applications in which the distinguishing features of ultrafine diamond are fully used. Some tentative examples that could be mentioned include use as electronic materials in which the nano-scaled sizes of the particles may display unique properties, as carriers for catalysts or sensors (including chemical and biosensors) in which the surface functional groups are important features, as filler in high polymer composites in which surface functional groups are also a crucial factor, as biomedical materials in which chemical inertness and biological compatibility are the most important

advantages, and many others. In short, ultrafine diamond, as a new kind of synthetic diamond, possesses a series of unique properties so new important applications can certainly be developed.

6.4. Perspectives

Explosives, as a special kind of material, can produce a special state of materials—detonation. In a long historical period of time, explosives have been used for the purposes of destruction, elimination, or decomposition, and these purposes still account for the main utilization of explosives. In recent years it has been found that explosives can be used for the opposite purposes of construction, creation, and synthesis. Using the high pressure, high temperature and high mass speed produced by explosive detonation, new substances or substances with unique features can be produced. Two examples are given in this chapter: shock-wave-induced chemical reactions for material synthesis and ultrafine diamond synthesized by explosive detonation. Much research work has been done in these fields in recent years, but the quantity and the depth of these studies are far from sufficient. There remain many unsolved problems and unexplored fields.

It is possible to realize new chemical reactions and synthesize new materials using shock-wave processing. Under the action of shock waves the particle velocity of reactants can reach an order of 1000 m/s, which approaches the vibrational velocity of atoms in molecules. This makes it possible to induce chemical reaction directly, that is, to convert mechanical energy (high-speed motion) directly to chemical energy (formation or decomposition of chemical bonds). In addition, besides the usual methods of explosive detonation and high-speed impact, strong shock waves can be easily produced by high-power lasers, which may open new possibilities in shock-wave chemistry. The production of ultrafine diamond by explosive detonation is another example, in which the nano-sized diamond particles can be synthesized by the action of shock waves on carbon-rich explosive molecules. Using a similar method, it is possible to synthesize other nano-scaled materials that are difficult or impossible to obtain by conventional methods. These few examples reveal the possibilities and prospects of shock-wave chemistry. Intensive and extensive research is needed for the better understanding and practical application of the results in these fields.

There are two main difficulties in the development of research work in shock wave chemistry. First, in order to understand the details of chemical reaction induced by shock waves, it is crucial to develop suitable *in situ* characterization techniques with high time resolution (at least to submicroseconds), high spatial resolution (to mm or, better, to μm), and high resolution for chemical species. These unsatisfied requirements must be met in order to achieve the identified research objectives. Since expensive, sophisticated instruments are necessary, a

large investment is required to carry out research of this kind. Second, the research in this field relates to many scientific disciplines, such as chemistry, physics, geology, gas dynamics, explosive science and techniques, materials science, scientific instrument research and development, etc., so the cooperation of scientists and technicians of different specialties is crucial. Unfortunately, such cooperation is not easily organized.

At the end of this chapter, we would like to appeal to more scientists and technicians of different specialties to take part in the research work of shock-wave chemistry in close collaboration in order to raise the research in this field to a higher level and to speed up the practical utilization of the achievements in these fields.

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