[Communication]

A New Method for Deaggregation of Nanodiamond from Explosive Detonation——Graphitization-Oxidation Method

Xu Kang Xue Qun-Ji

(*State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000*)

Abstract Nanodiamond (ND) prepared by explosive detonation has primary particles of 4 ~ 6 nm in diameter, but it undergoes severe aggregation in forming aggregates of hundreds of nm, even several μm in diameter. A new method for the deaggregation of nanodiamond (ND) is developed and some preliminary results using this method are presented: ND is first graphitized in nitrogen at 1 000 ℃ during which thin graphite layers are formed on the surface of the diamond particles and at the particle boundaries. The sample is then oxidized by air at 450 ℃ to remove the formed graphite layers. After such treatment the sample is suspended in water by ultrasonics, and the particle size distributions were measured by the laser scattering method. It has been found that the diameter of about 50% (w) of the ND particles can be reduced to less than 50 nm, while such ultrafine particles are absent in the suspension of the untreated ND. It is suggested that the deaggregation is caused by the removal of the graphite layers formed at the particle boundaries in the stage of oxidation. It is also found that after oxidation, some aggregates with larger diameters (1 000 ~ 2 000 nm) are formed, which can be explained by the formation of inter-particle ethereal bondings (C – O – C) during the oxidation by air.

Keywords: Nanodiamond (ND), Deaggregation, Graphitization, Oxidation

Nanodiamond (ND) prepared by explosive detonation is a unique sort of synthetic diamond[1-4]. One distinct feature of this kind of diamond is that the diameters of the primary particles are in the range of 4 ~ 6 nm[5], but a large number of nanoparticles aggregate to form fractal clusters with diameters of hundreds of nanometers, or even of several micrometers. The nature of the aggregation of ND is not clear. Many works dealt with the deaggregation of ND, but monodispersion has not been achieved up to now. When ND is dispersed in water by ultrasonics, only a small portion of the ND powder can be transferred into particles with diameters less than 100 nm[6].

As accepted by many researchers, in nano-materials there are two kinds of aggregation: the "soft aggregation" caused by the adsorption of particles and the "hard aggregation" caused by chemical bonding between particles. But, in our opinion, a third kind of aggregation exists in ND.

From the HRTEM images of ND [5], it is evident that each nano-sized particle is a single crystallite of diamond and between two crystallites there is an unclear boundary. We believe that this is, perhaps, a co-crystalline phase or an amorphous diamond-like carbon (DLC) between the two crystallites, which causes the aggregation of the particles. We call this kind of aggregation "ultrahard aggregation", which is much stronger than the other two. Apparently, it is impossible to deaggregate such bonding between diamond crystallites by ordinary physical or chemical methods.

Kuznetsov *et al.* [7-8] reported that the HRTEM images of ND heat-treated at temperatures higher than 1 000 ℃ in vacuum show that graphitization happens on the surface of ND crystallite. We deem that when two diamond crystallites bound together by a co-crystalline or an amorphous DLC boundary region is heat-treated, a graphite layer could be formed on their surfaces and boundary regions. Now if we can use some oxidation methods to remove the graphite layer, then the "ultrahardly" aggregated diamond crystallites may be deagglomerated. We call this method "graphitization-oxidation method". Experiments of ND deaggregation using this new method have been carried out in our laboratory and some preliminary results are presented in this communication.

1 Experimental

ND powders were prepared by the detonation of 50/50

Received: July 21, 2003; Revised: September 6, 2003. Correspondent: Xu Kang (E-mail: kangxu@lsl.ac.cn; Tel: 0931-8277348)

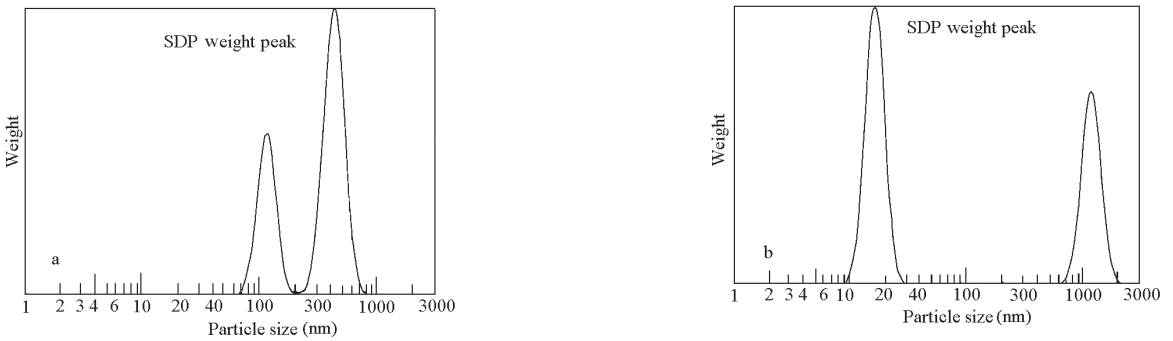

Fig. 1 Particle size distribution of aqueous suspensions prepared from original ND (a) and from ND after graphitization-oxidation treatment (b)

TNT(trinitrotoluene)/RDX(trimethylene trinitramine) explosive charge using water as the cooling and protecting medium[3]. For graphitization, the ND was heat-treated in N_2 at 1 000 ℃ for 1 h, after which the color of sample changed to dark black indicating graphitization occurred. For oxidation, the sample is treated in an air flow at 450 ℃ for about 2 h, at this time the black color of the graphitized diamond particles faded and the original color of ND completely recovered. So we can confirm that the graphitization of ND at 1 000 ℃ for 1 h only produced a thin layer of graphite on the surface of ND crystallites.

The ND sample after graphitization - oxidation treatment was dispersed in water with a concentration of 0.5% by ultrasonics. The particle size distributions of ND in the obtained suspensions were measured on a N-4 Plus dynamic laser scattering apparatus (Coutler Co.). TEM images were recorded on a JEM-2010 transmission electron microscope. IR spectra were recorded on a Bio-Rad FTS-165 IR spectrometer.

2 Results and discussion

The particle size distributions of the aqueous suspensions prepared from the original ND and the sample treated by graphitization-oxidation are shown in Fig. 1. It can be seen that in the suspension of the ND after graphitization-oxidation treatment, about 50% of the particles have diameters less than 50 nm [see Fig. 1b], which is absent in the suspension of the untreated ND [see Fig. 1a]. So it is believed that the graphitization-oxidation method has some effect on the deaggregation of ND.

The HRTEM images of the untreated and treated ND are shown in Fig. 2. After graphitization only a single black circle is formed around the diamond nano-crystallites (see Fig. 2a), which disappears after oxidation (see Fig. 2b). From these results it can be concluded that during graphitization a portion of the diamond crystallites is converted to surface graphite layers, which are converted to gaseous products in the stage of oxidation. During this process some "ultrahard" aggregates were deaggregated.

But it can also be seen from Fig. 1b that after graphitization-oxidation treatment some particles with larger diameters (1 000 ~ 2 000 nm) are formed.

The samples were also examined by FTIR spectrometry. From the spectra, we can see that the characteristic band of ethereal group (C – O – C) (~1 100 cm^{-1}) enhanced after graphitization and oxidation, indicating that more bridged oxygen bonds are formed, which may result in the formation of agglomerates with larger diameters. If our above suggestion is correct, it means that during graphitization and oxidation, more "hard aggregation" are formed, that is, the aggregates formed by inter-particle ethereal

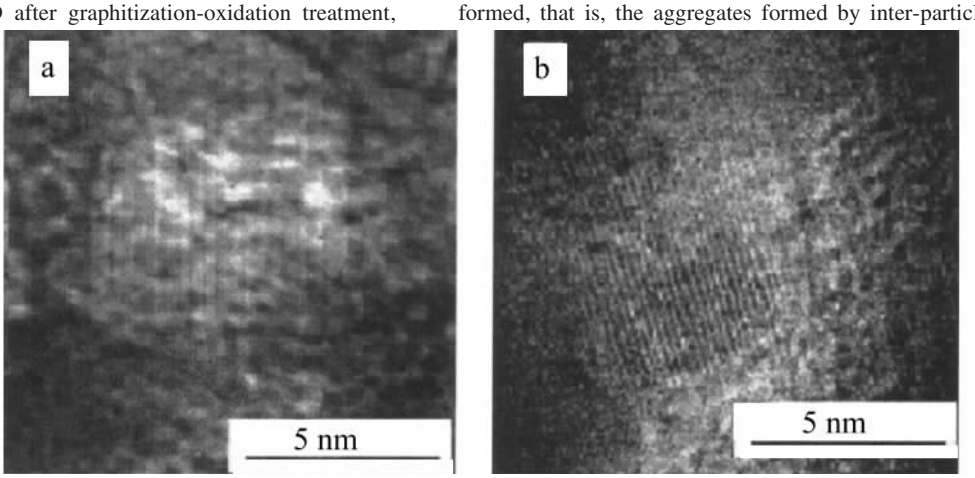

Fig. 2 HRTEM images of ND after graphitization (a) and after oxidation (b)

bridged oxygen bonds. We deem that in order to deaggregate such kind of bonding some suitable chemical reactions must be used to cleavage the inter-particle ethereal bonding. Experimental work in this aspect is in progress in our laboratory and the results will be published later.

3 Conclusion

A new method for the deaggregation of nanodiamond(ND) prepared by explosive detonation is developed. In this method the ND is first heat-treated to set off surface graphitization, and then air oxidation is used to remove the thin surface graphite layer. So this method is called the "graphitization-oxidation" method. The preliminary experimental results of deaggregation of ND using this method indicate that it has some positive effects on the deaggregation of ND. Since the graphitization-oxidation process is rather complicated, further investigation is needed to verify the mechanism and usefulness of this method.

References

1 Gneiner, N. R.; Phillips, D. S.; Johnson, J. D.; Volk, F. *Nature,* **1988, 333**: 440

2 Lyamkin, A. E.; Petrov, E. A.; Ershov, A. P.; Sakovich, G. V.; Staver, A. M.; Titov, V. M. *Doklady Akad. Nauk. SSSR*, **1988, 302**(3): 611

3 Xu K., Xue, Q. J. *Progress in Chemistry*, **1997, 9**(2): 201 [徐康, 薛群基. 化学进展 (*Huaxue Jinzhan*), **1997, 9**(2): 201]

4 Dolmatov, V. Y. *Russ. Chem. Rev.*, **2001, 70**(7): 607

5 Xu, T.; , Xu, K.; , Zhao, J. Z. *Mater. Sci. Eng. B,* **1996, B38**(1): L1

6 Agibalova, L. V.; Voznyakovskii, A. P.; Dolmatov, V. Y.; Klyubin, V. V. *Sverkhtvd. Mater.,* **1998,** (4): 87

7 Kuznetsov, V. L.; Chuvilin, A. L.; Butenko, Y. V.; Mal′kov, I. Y.; Titov, V. M. *Chem. Phys. Letters*, **1994, 222**(4): 343

8 Butenko, Y. V.; Kuznetsov, V. L.; Chuvilin, A. L.; Kolomiichuk, V. N.; Stankus, S. V.; Khairulin, R. A.; Segall, B. *J. Appl. Phys.,* **2000, 88**(7): 4380

纳米金刚石解团聚的一种新方法——石墨化 - 氧化法

徐 康 薛群基

(中国科学院兰州化学物理研究所,固体润滑国家重点实验室,兰州 730000)

摘要 用炸药爆炸法制备的纳米金刚石(ND)是由直径为 4 ~ 6 nm 的金刚石微晶粒组成,但这种纳米晶粒相互团聚,形成尺寸大得多的团聚体,至今尚未找到很有效的解团聚方法. 该文提出了一种可用于这种纳米金刚石解团聚的新方法——石墨化 - 氧化法. 将纳米金刚石粉在氮气中 1 000 ℃加热 1 h,这时纳米颗粒表面和界面上生成石墨层,再用在空气中 450 ℃氧化的方法,将界面上的石墨层除去. 将经过这样处理后的样品放入水中用超声波分散后,超过 50% (质量百分数)的金刚石颗粒可以被分散到直径小于 50 nm. 可见这种方法对纳米金刚石的解团聚有一定的效果. 但是同时也生成了一部分尺寸更大的团聚体,认为可能是生成了颗粒间的 C – O – C 键,需要进一步用适当的化学方法进行解离. 对这一过程的机理进行了初步讨论.

关键词: 纳米金刚石, 解团聚, 石墨化, 氧化

中图分类号: O648

2003-07-21 收到初稿,2003-09-06 收到修改稿.

联系人:徐 康(E-mail: kangxu@lsl.ac.cn; Tel: 0931-8277348)