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Property Comparison of Porous Graphite Nanopowders Prepared by Detonation Splitting Technique with Different Acid Content*

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Abstract: N_2 adsorption/desorption isotherms and pore diameter distribution of the porous graphite nanopowders, prepared by detonation splitting technique with different acid content in raw materials, were analyzed using Brunauer-Emmet-Teller(BET) equation and Barrett-Joyner-Halenda(BJH) method. The results indicate that there exists hysteresis phenomenon in the product isotherms and the corresponding BET surface area is 5.3～9.2 times of the natural flake graphite which is increasing with the acid content in raw materials. The difference of the BET surface area among the detonation soot is mainly caused by the pore of which diameter distributes between 3 nm and 7 nm. Moreover, the amount of the pore size at about 4 nm arrived at the maximum after detonation. In addition, the research provides sorption capacity information for application and at the same time it also proves that acid has perfect impact on preparing graphite nanopowders.

Key words: graphite nanopowders; adsorption/desorption isotherms; pore size distribution; detonation technique

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1 Introduction

Graphite has been under investigation for decades, it is still a scientifically highly interesting material which exhibits the properties both of a metal, such as thermal and electrical conductivity, and of a non-metal such as inertness and lubricity. Moreover, graphite nanopowders can be used as an additive of lubricating oil, which would adsorb oil and give better lubricate property[1]. Till now, graphite nanopowders have been prepared by lots of methods, such as milling[2-3], detonation[4-6], ultrasonic[7] and chemical synthesis[8-9]. Each method has its own advantage and shortcoming. Comparatively, detonation technique has the advantage of high-efficiency and energy-saving. Accordingly, it has been used for graphite nanopowders preparation in recent years. Wen, et al.[4] synthesized graphite nanopowders by detonating TNT with shielding gas as carbon dioxide, argon and nitrogen or in vacuum. Li, et al.[5-6] split natural graphite and exfoliated graphite to prepare graphite nanopowders by detonation technique. This kind of detonation technique utilized the unique structure of graphite, the strong sp^2 carbon-carbon bonding within a layer and weak van der Waals bonding between adjacent sheets, and the carbon hexagonal net could host a number of molecules while it maintained its own layer integrity. The breakdown of the intercalates played a crucial role in forming graphite nanopowders.

We compared the property of porous graphite nanopowders via analyzing the BET(Brunauer-

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Emmet-Teller) surface area and pore size distribution(PSD) and studied the effect of acid on the graphite nanopowders. The analysis of the sorption capability and PSD of the detonation soot provides more information about graphite nanopowders for the potential application.

2 Experiment

2.1 Materials

Natural flake graphite(NFG) and expendable graphite, concentrated HNO_3, $(CH_3CO)_2O$, hexahydro-1,3,5-trinitro-1,3,5-triazine(RDX), 2,4,6-trinitrotoluene(TNT). Herein, expendable graphite was prepared using NFG mixed with 97% H_2SO_4 and fuming nitric acid in a volume ratio of 2 ∶ 1 according to the methods reported in the Ref. [10].

The agents were of analytical purity and used without pre-treatment. Three detonation experiments were carried on in the explosion vessel(Fig. 1).

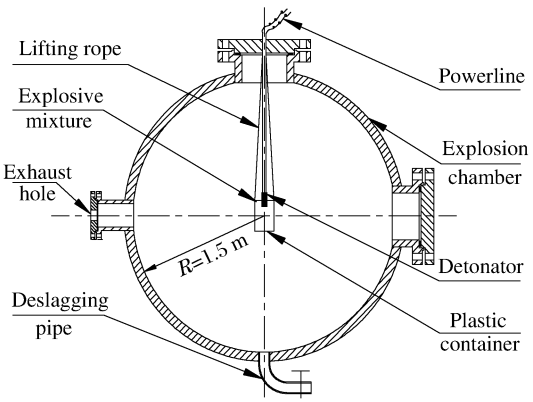


Fig. 1 The schematic of explosion vessel

2.2 Procedure

Approach 1(App-1): The expandable graphite was used as raw material and mixed with RDX adequately in a weight ratio of 2 ∶ 3. Then, the mixture was put into a plastic container which was subsequently put into the centre of the explosion vessel. And the reaction was initiated by a detonator in the explosion vessel.

Approach 2 (App-2): NFG was used as raw material and mixed with concentrated HNO_3, $(CH_3CO)_2O$ and TNT in turn in a weight ratio of 1 ∶ 3 ∶ 0.5 ∶ 2. The obtained mixture was pasty. Then the paste was loaded into a plastic container and was initiated by a detonator.

Approach 3(App-3): NFG was used as raw material and mixed with concentrated HNO_3 and CH_3NO_2 in turn in a weight ratio of 1 ∶ 5.25 ∶ 10.1 in cool water bath(0～20 ℃). The obtained mixture was liquid. Then the blended liquid was poured into a plastic container and initiated by a detonator.

After detonation, the soot-like deposits were collected from the inner surface of the explosion vessel. The isotherms of NFG and three kinds of detonation soot were determined using the BET equation while PSD using the Barrett-Joyner-Halenda(BJH) method by AutoChem2910(Nitrogen adsorption at 77 K). Thermo Gravimetric Analysis(TGA) was used to study the decomposing temperature of the mixtures from App-1 to App-3.

Expandable graphite was used as raw material in App-1, mixed with RDX and formed an explosive powder mixture while the mixture in App-2 was an explosive paste. And the explosive mixture prepared in App-3 was liquid.

3 Results and Discussion

Fig. 2 shows that there exist sorption hysteresis phenomena in the N_2 adsorption-desorption isotherms. Herein, hysteresis effects observed in isotherm experiments are related to the pore structure of the graphite. The hysteresis loop of the detonation soot from App-3 is the most obvious one. And the

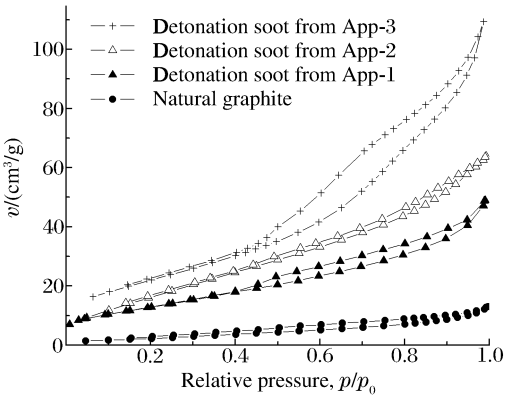


Fig. 2 Isotherms of NFG and three kinds of detonation soot (The lower branch of each materials is for adsorption isotherm while the upper is desorption isotherm)

loops from three kinds of detonation soot were all started at about $0.42p_0$ and ended at p_0 while NFG started at about $0.2p_0$ and ended at p_0. Because the pore of same size has the same property, it is easy to understand that the phenomenon that the hysteresis loop of the detonation soot became shorter than NFG is resulted from the convergent pore size distribution. That is to say, the isotherms also reflected the range of the pore size distribution and indicated that the pore diameter after detonation became more uniform than before.

The pore diameter distribution was determined using BJH method. Fig. 3 shows the desorption volume of the same pore diameter drastically increased after detonation. And it also gave the information that the increase of BET surface area was mainly caused by the pores whose diameter distributes between 1.5 nm and 10 nm. The detonation soot from App-1, App-2 and App-3 herein shows the desorption of the pore below 3 nm decreased gradually but not obvious. However, when the diameter is greater than 3 nm, a clear distinction that the desorption volume increased at steep slope presented. And at about 4 nm, the desorption volume reached the maximum. That is to say, detonation technique has the most significant influence in increasing the amount of the pores with the diameter around 4 nm. Moreover, the desorption of the pore size greater than 4 nm is all increased though it mainly distributed between 3 nm and 8 nm.

The BET surface area of NFG and three kinds of detonation soot, determined by BET equation, are listed in Table 1.

Table 1 BET surface area of the graphite

Graphite source	BET surface area/(m^2/g)
NFG	8.92
App-1	47.48
App-2	66.54
App-3	81.74

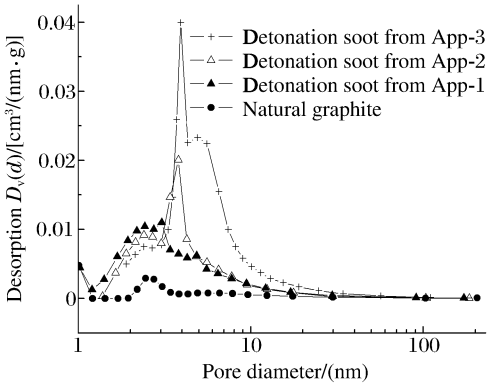


Fig. 3 Pore diameter distribution

It shows that the detonation soot from App-1 is the least increased one which is 5 times of NFG while the soot from App-3 is 9 times of NFG, which gives the information that the detonation soot increased greatly in BET surface area. It is because pristine graphite has the property of hosting layers of foreign atoms and forming Graphite Intercalation Compounds(GICs). Herein, one of the most remarkable structural features in GICs is a unique *c*-axis periodicity of the graphitic galleries in which intercalation are accommodated and occupied graphitic galleries periodically in the *c*-axis direction[11]. The more graphitic gallery the intercalation occupied, the thinner the graphite nanopowders became. The preparation of the graphite nanopowders by detonation is based on the breakdown of the intercalation, which gives off lots of gases to burst the adjacent graphite layers open immediately and results in

big BET surface area. In these experiments, the more completely the graphite split, the bigger the BET surface area will become. So, the graphite in App-3 before detonation owns the biggest BET surface area. At the same time, it indicated that intercalation increased with the increasing acid content in the mixture.

The mixture from App-1 to App-3 is powder, paste and liquor respectively. And the acid content was obviously elevated. The ratios of graphite to intercalation or acid in three approaches are listed in Table 2.

Table 2 Ratios of graphite to intercalation

Methods	Graphite to intercalation
App-1	1 : 0.08
App-2	1 : 3.00
App-3	1 : 5.25

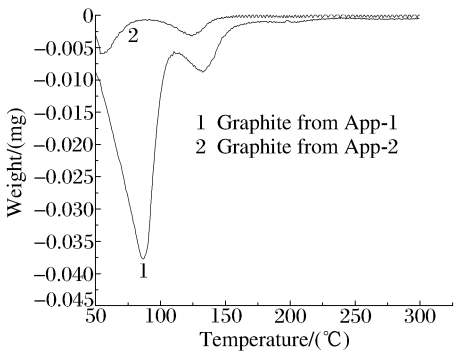


Fig. 4 TGA of expandable graphite and GICs

TGA was used to get the decomposing temperature to provide proof for the pertinence of acid. In App-2 and App-3, the difference between them is the amount of intercalation hence the decomposing temperature is similar. Fig. 4 indicates that the decomposition started below 50 ℃ and completed at about 160 ℃ so that the composition of the explosive had no influence on the detonation soot because of high detonation temperature above 2 000 K[12-13].

4 Conclusions

Graphite nanopowders were prepared with the raw materials in three states: powder, paste and liquid. With the varying condition in those experiments, the acid content is increasing. The BET surface areas of the graphite nanopowders prepared by detonation technique in three experiments were enlarged with the increasing acid content, which has little effect on the pore size amount distributing below 3 nm through detonation method while it has great effect on the pore size greater than 3 nm, especially between 3 nm and 8 nm. Moreover, the amount of the pore size distributing around 4 nm arrived at the maximum after detonation.

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爆轰裂解法制备纳米石墨粉的吸附性能研究

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摘要: 在酸含量不同的原材料中,通过爆轰的方法制备纳米石墨粉,并利用 BET 方程以及 BJH 方法对所得纳米石墨粉进行比表面积和孔径分布分析。分析结果表明,所得爆轰产物中有的比表面积大致为天然鳞片石墨的 5.3～9.2 倍,而且随酸含量的增大逐渐增大,产物的等温线中存在吸附滞后现象。其中,增大的比表面积主要由分布在 3 nm 至 7 nm 之间的孔引起的,而且在爆轰后,孔径 4 nm 左右的孔,其数量达到最大值。通过对纳米石墨粉的研究,分析了酸在爆轰过程中的积极作用,并为纳米石墨粉的进一步应用提供了结构信息。

关键词: 纳米石墨粉;吸附/脱附等温线;孔径分布;爆轰技术

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