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Fixed carbon content and reaction mechanism of natural microcrystalline graphite purified by hydrochloric acid and sodium fluoride

Wei Xie [a,b,c,*], Zhen Wang [a,b], Jiacai Kuang [a], Hua Xu [a,b], Shihe Yi [c], Yingjun Deng [a], Taishan Cao [a,b], Zhanhu Guo [d]

[a] Hunan Province Key Laboratory of Safety Design and Reliability Technology for Engineering Vehicle, Changsha University of Science & Technology, Changsha 410114, China
[b] Hunan Province Higher Education Key Laboratory of Modeling and Monitoring on the Near-Earth Electromagnetic Environments, Changsha University of Science & Technology, Changsha 410114, China
[c] College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, China
[d] Chemical and Biomolecular Engineering Department, University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

In order to improve the fixed carbon content of microcrystalline graphite (MG) and broaden its application, this article discussed the fixed carbon content and purification reaction mechanism of natural MG by using hydrochloric acid and sodium fluoride. The influence of sodium fluoride amount, liquid-solid ratio, reaction temperature and reaction time were respectively investigated using MG as raw materials. Results indicate that the fixed carbon content of MG increased with the increasing amount of fluoride; with the increment of the liquid-solid ratio, reaction temperature, and reaction time. In all cases, the fixed carbon content significantly increased at first then slowed down its increasing rate. The fixed carbon content of MG can be increased from 83.08% to 98.37% when 13.5 g sodium fluoride amount and 30 g microcrystalline graphite reacted with 120.5 ml hydrochloric acid at 70 °C for 2.5 h. Hydrochloric acid can be used to convert the impurities such as metal compounds into soluble chloride. Hydrofluoric acid generated from sodium fluoride removes most of the complex silicate impurities, and then to be washed and filtered to achieve the separation of graphite. The crystal structure and morphology of MG will not be changed according to the SEM images and the XRD patterns. Results indicate that the hydrochloric acid and sodium fluoride method can enhance the fixed carbon content of MG to a higher level.
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1. Introduction

On earth there is massive storage of natural graphite minerals, including flake graphite and microcrystalline graphite (MG). The former mineral usually contains flake graphite with crystal size larger than 10 μm, however, the concentration of carbon is very low. In contrast, the latter usually has a small crystal size of < 1 μm but a high carbon content (Wang et al., 2015). There are large and widespread deposits of natural MG in China. The largest mine, with a reserve of 30 million tons, is located in the Lutang area of Chenzhou, Hunan province. Other major deposits are known in the provinces of Inner Mongolia (Bayan Nur), Hubei (Shiyan), Fujian (Sanming), Jilin (Panshi), and Heilongjiang (Yichun). The grade of some European deposits is about 55%, while counterpart of some MG deposits in China is 50%–85% (Shen et al., 2015).

MG, as a kind of resourceful and cheap natural graphite with high degree of graphitization and micro-polycrystals with different orientations, was inefficiently utilized and seriously wasted due to the low-level technical process in China. The utilization of MG is currently confined to a preliminary level such as raw materials for pencil lead, crucible, and carburant for steel making. Investigations into further applications of MG will greatly promote the development of the MG industry in China (Shen et al., 2013; Wang et al., 2014a,b). Wang Junying and coworkers (Wang et al., 2015) produced high-quality graphene microsheets at a high yield of > 70% through a scalable electrochemical & mechanical exfoliation approach using natural MG minerals directly. Xian Haiyang and coworkers (Xian et al., 2015) prepared graphene nanosheets (MGS) from MG by a low-temperature (as low as 100 °C) exfoliation method, and the supercapacitive behaviors of the MGS have also been investigated. Shen Ke and coworkers (Shen et al., 2015) proposed the approach of preparing isotropic graphite using MG fillers. Recently MG has been applied as anode material of lithium-ion battery (Cameán, Garcia, 2011; He et al., 2013; Kim et al., 2014; Lin et al., 2014; Park et al., 2013; Wang et al., 2008; Xiao et al., 2013; Yu et al., 2015), refractory (Wang et al., 2014a,b), supercapacitor (Laurence et al., 2006; Deylová et al., 2014) as a cheap and abundant resources. Specifically, the usage of the lithium-ion battery is increasing drastically, therefore, a large number of submicron or nano-carbon sources with high fixed carbon content, large surface area, high activity, and high thermal conductivity should be developed to meet the demand of the industrial applications aforementioned.

* Corresponding author.
E-mail address: xwxw00@163.com (W. Xie).

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Table 1
Chemical compositions of natural MG minerals (wt%).

Index	C	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	Ka_2O	MnO_2
Content(%)	83.08	5.95	3.39	0.44	0.40	0.30	0.043	0.26	0.41	0.0097

There are two main development trends of MG products in modern industry, one is the high purity (purity ≧ 99.9%) and the second is the ultrafine particles (size <1 or 0.5 μm). To obtain high-purity natural graphite, purification treatment plays an important role in the modification process. The impurities of natural MG include quartz, silicate minerals, aluminum oxides, magnesium, calcium and other non-graphite components. These impurities are difficult to be removed in the purification process because the concentration is pretty high and they are disseminated with fine granularity in MG. A number of research projects have been undertaken so far, purifying the graphite by physical and chemical treatment. Physical methods include flotation and high temperature purification method (Ge et al., 2010a,b; Li et al., 2013, 2014; Liu, 2000). Chemical methods include alkaline-acid method, hydrofluoric acid method, and chlorination-roasting method (Ge et al., 2010a,b; Ge et al., 2011; Li, Yao, 1996; Lu, Forssberg, 2002; Niu et al., 2011; Tang et al., 2012; Tang et al., 2013; Zhang et al., 2005). Among these purification technologies, flotation method is low-cost, but it is difficult to obtain MG with a fixed carbon content of >95%. According to the characteristics of high temperature resistance of graphite, low boiling point impurities of natural MG are volatilized at high temperature if it is treated by the high temperature method. This method is only suitable for the production of high purity graphite (purity > 99.9%) because the high temperature method is expensive and the scope of application is narrow. Alkali-acid and chlorination-roasting method can greatly improve the purity. However, the energy consumption is large and the equipment corrosion is serious, also the process is complex. Hydrofluoric acid method can remove the impurity with high efficiency and low energy consumption, but hydrofluoric acid is corrosive, toxic, and harmful to the environment as well as human health. Therefore, it is necessary to optimize the purification process conditions so as to reduce environmental pollution.

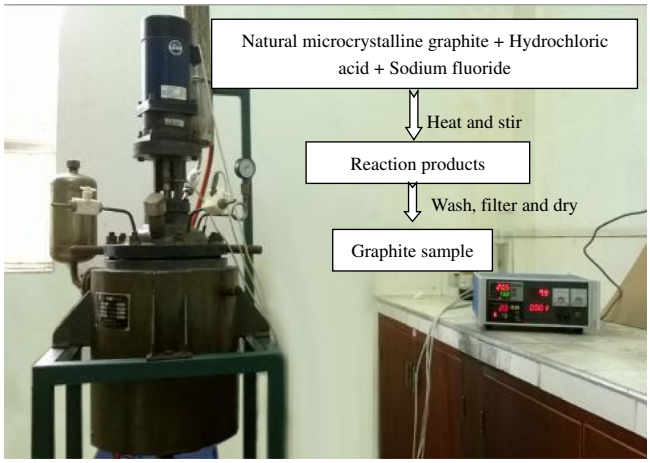

Fig. 1. The flow diagram and reaction equipment of natural MG purification treatment.

This work aims to optimize the chemical purification agent system of hydrofluoric acid method, as far as possible to reduce the influence on the environment. Based on the theory of hydrolysis reaction, our purification method using both sodium fluoride and hydrochloride acid has less damage to environment without sacrificing the high purification efficiency. Furthermore, it effectively compensates for the disadvantages of hydrofluoric acid purification method (Kuang et al., 2013). Therefore, this article studies the chemical purification process of natural MG by hydrochloric acid and sodium fluoride, and investigates the technological parameters on the fixed carbon content and reaction mechanism based on our previous work.

2. Experimental

2.1. Purification treatment

Natural MG minerals (chemical compositions presented in Table 1) with approximately 83.08 wt% fixed carbon content were used as raw materials, obtained from in Chenzhou, Hunan province, China. Large pieces of natural MG minerals were crushed and dry-grounded by jaw crusher. To improve the purification reaction activity and efficiency, the ground mineral particles were dry-screened using the standard sieve (160 mesh) and the natural MG minerals with narrow particle size distribution were used as reagents in the chemical purification process. Hydrochloric acid (37%) and sodium fluoride (98%) were purchased from Hengyang Kaixin Chemical Reagent Co. Ltd. and Changsha Minle Chemical Co., Ltd. These chemicals were used without further purification. The reaction kettle was designed by ourselves and made by Weihai Huanyu Chemical Machinery Co. Ltd.

The illustration for the purification process can be seen in Fig. 1. First, the natural MG minerals, sodium fluoride and hydrochloric acid were successively put in the reaction kettle. Then, the raw materials were stirred and mixed by a stirrer in the reaction kettle with the rotating speed of 80–100 rpm at 30–90 °C for 0.5–3.5 h, which initiated the chemical reactions. After reaction, the reaction kettle was cooled in the air to room temperature and the sample was taken out from the reaction kettle, washed, filtered and then dried in a heated blast oven. All factors and their ranges are listed in Table 2.

2.2. Test and characterization methods

2.2.1. The test of fixed carbon content

According to the standard method (Method for chemical analysis of graphite) in China (GB/T 3521-2008, 2009), the technical analysis (volatile matter, fixed carbon content and ash) of MG single mineral was done in the Changsha Research Institute of Mining and Metallurgy in Hunan province, China. Muffle furnace was used to determine the volatile matter and fixed carbon contents of samples. Fixed carbon is the solid combustible residue that remains after heating of MG particle at 900–1000 °C for 1 min and the expelling of volatile matter. The fixed carbon content of a MG is determined by subtracting the percentages

Table 2
Factors and their ranges of the experiment.

Factors	Sodium fluoride amount (g)	Liquid-solid ratio[a]	Reaction temperature (°C)	Reaction time (h)
Ranges	3, 4.5, 6, 7.5, 9, 10.5, 11.25, 12, 12.75, 13.5	1.5, 2, 2.5, 3, 3.5, 4	30, 40, 50, 60, 70, 80, 90	0.5, 1, 1.5, 2, 2.5, 3, 3.5

[a] Liquid-solid ratio: the ratio of liquid volume to solid material mass.

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