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Preparation of exfoliated graphite intercalated with nitrogen dioxide by direct gas-phase processing

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ABSTRACT

Graphite intercalation compound (GIC) as a precursor of exfoliated graphite (EG) was easily prepared by direct reaction of nitrogen dioxide gas with natural flake graphite (NFG). This preparation involved a one-step method under optimum conditions of 55 °C and 0.45 MPa for 48 h in a dry, sealed steel container. The maximum exfoliation volume (EV) of EG was up to 240 ml g^{-1} with the exfoliated method at 1000 °C. A comparative study of properties and microstructure distinctions between GIC and EG samples was carried out using scanning electron microscopy, thermal gravity analysis, and differential scanning calorimetry coupled with Fourier transform infrared spectroscopy. The influence of reaction condition on the property, structure, and EV of the EG was also discussed.

1. Introduction

Exfoliated graphite (EG) is widely used for manufacturing flexible graphite [1], thermal energy storage materials [2], SBR composites [3], sorbents [4–5], fire extinguisher agents [6–7], and thermal insulators [8]. Graphite intercalation compound (GIC) as a precursor for EG has been studied using various intercalating agents, namely, sulfuric acid [9–11], nitric acid [12–14], perchloric acid [15], hexachloroplatinic acid [16], and so on. Natural flake graphite (NFG) is treated with strong oxidizing solutions or mixtures such as sulfuric acid, potassium permanganate, and nitric acid, to expand the interplanar spacing of graphite for intercalation. GIC can be obtained in a wet complicated process and hydrolyzed by distilled water, resulting in EG. However, safe treatment of strong corrosive acid wastes or mixtures is difficult to achieve. Thus, searching for easy and direct routes for the preparation of EG is important.

Nitrogen dioxide (NO_2) gas is a major component that a liquid propellant, both dinitrogen tetroxide and green dinitrogen tetroxide, releases at high temperature. This study reports, for the first time, an easy and straightforward route for preparing EG with NO_2 by gas-phase processing [17]. NO_2 gas serving as both an oxidant and intercalating agent can react directly with NFG by a one-step method in a dry, sealed steel container. In this study, recovery and recycling of residual NO_2 gas establishes an easy and effective route for the safe treatment of waste nitro oxidizer propellant. A comparative study of the properties and microstructural distinctions between GIC and EG samples is carried out by scanning electron microscopy (SEM), thermal gravity analysis, and differential scanning calorimetry coupled with Fourier transform infrared spectroscopy (TG–DSC–FTIR). The influence of reaction condition on the exfoliation volume (EV) of EG is also discussed, and the optimum conditions are obtained.

2. Experimental

Preparation of GIC: A sealed reaction container made of steel 304 was vacuumed less than 300 Pa after 15 g of NFG (99.9 wt%, 50 meshes) was added. NO_2 gas was charged into the reaction container by a gas booster with various pressures to react with NFG at different temperatures above 25 °C, and then heated in an oil bath for 24, 48, and 72 h. GIC was obtained, washed with distilled water, and dried in an oven at 60 °C. Residual NO_2 gas was discharged through an evacuation valve for recovery and recycling.

Caution: NO_2 gas is a strong oxidant with high toxicity; thus, safety protective devices must be used during the preparation.

Preparation of EG: An appropriate amount (to the accuracy of 0.001 g) of GIC sample was placed into a quartz beaker that had been heated for 5 min. The beaker with GIC sample was then immediately placed into a high-temperature furnace of 1000 °C with the door open. When the expansion of the sample stopped, the beaker was removed.

Measurement of EV: According to the Chinese National Standard GB 10698-1989, the EV was measured as follows. EG

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was gently transferred into a 100 ml graduated cylinder, and the volume (V) occupied and quality (M) of EG were recorded. The EV was calculated by the following equation: $EV = V/M$ (ml g^{-1}).

3. Results and discussion

The factors of orthogonal experiments and the EV results of EG under different reaction conditions are shown in Table 1. The

Table 1
Orthogonal experiment results of EG.

No.	Factors			Exfoliation method	EV (ml g^{-1})
	A – reaction pressure (MPa)	B – reaction temperature (°C)	C – reaction time (h)		
1	0.45	65	24	Heating, 1000 °C	110
2	0.45	55	48	Heating, 1000 °C	240
	0.45	55	48	Heating, 900 °C	220
	0.45	55	48	Heating, 800 °C	190
	0.45	55	48	MW (800 W, 60 s)	210
	0.45	55	48	MW (600 W, 60 s)	180
3	0.45	45	72	Heating, 1000 °C	230
4	0.35	65	48	Heating, 1000 °C	130
5	0.35	55	72	Heating, 1000 °C	185
6	0.35	45	24	Heating, 1000 °C	160
7	0.25	65	72	Heating, 1000 °C	100
8	0.25	55	24	Heating, 1000 °C	170
9	0.25	45	48	Heating, 1000 °C	160
K_1	600	340	440		
K_2	475	595	530		
K_3	430	570	525		
δ	56.7	85	30		
Optimum	A_1	B_2	C_2		

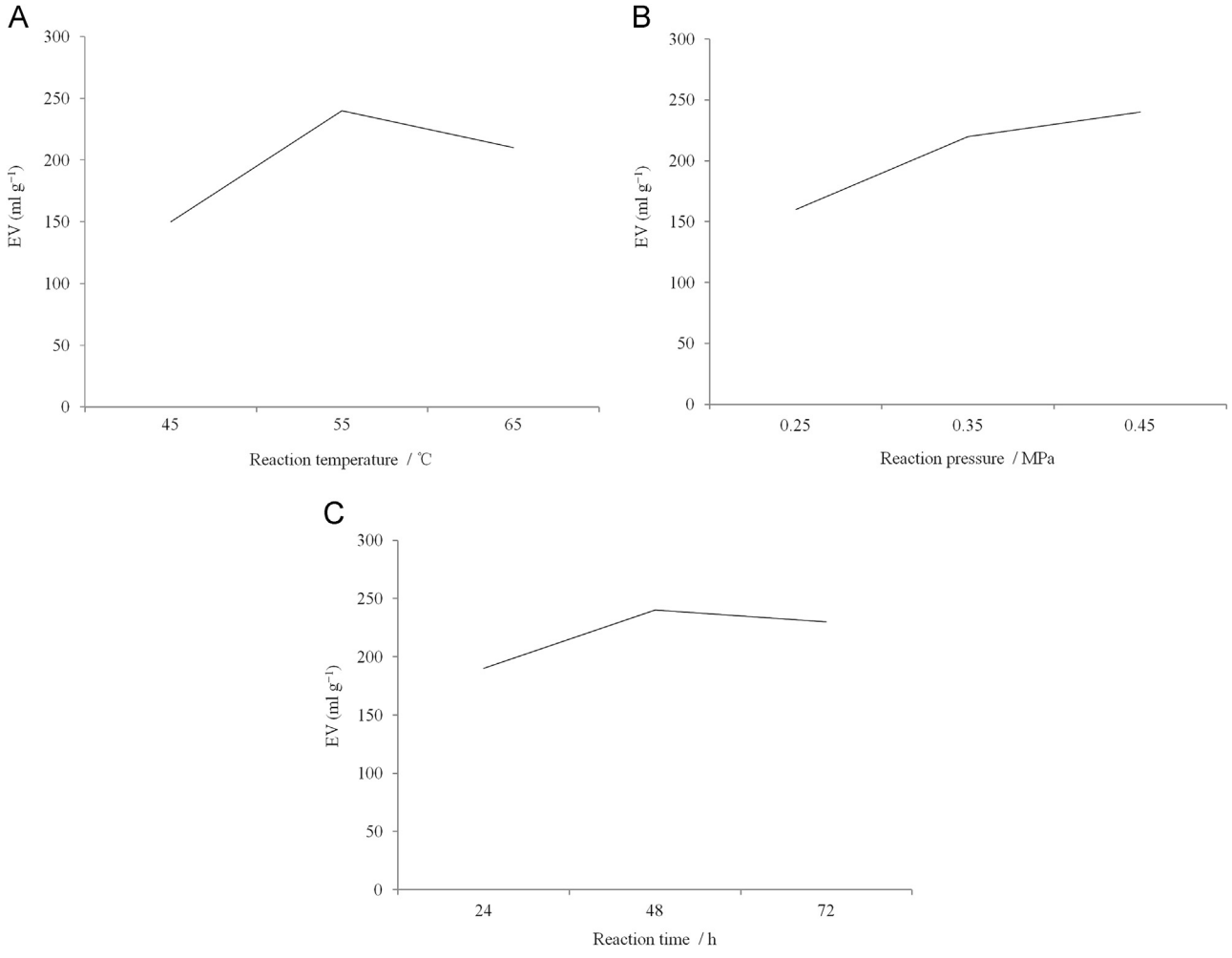

Fig. 1. EV variation as the function of (A) reaction temperature at 0.45 MPa with 48 h; (B) reaction pressure at 55 °C with 48 h; (C) reaction time at 55 °C with 0.45 MPa.