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Gravity and heat treatment influence in the graphite exfoliation

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Abstract

Exfoliation of graphite is a common method to get graphene. This technique is the most economic method to have graphene in larger quantities. In this work commercial graphite was mixed with $FeCl_3$, $KMnO_4$ and H_2SO_4 in an aqueous solution, after this treatment the GIC was heated at 10 min in different temperatures sets. The intermediary temperature set was made also at high gravity. The results show the formation of EG, but without exfoliation.

Keywords: high gravity; graphite exfoliation; GBC.

1. Introduction

Graphite is a material with some good physical and electrical properties, e.g.: high electrical conductivity, in spite of a low carrier concentration, high electrical anisotropy, high melting and boiling points. Its structure is layered, this allows the introduction of molecules or atoms between these layers or graphene planes. By a chemical reaction, this graphene planes can be separated, producing then the Graphite Intercalation Compounds (GICs). The GICs can be expanded in a worm-like structure known as expanded graphite (EG), with low density and large surface area. Many types of processing can be used for this expansion, by microwave irradiation or rapid heating[1,2].

The $FeCl_3$-H_2SO_4-GIC is a graphite bi-intercalation compound (GBC), the GBC is a GIC with two different intercalates occupying separated successive interspaces[3,4]. This compound has very reported about its preparation, mechanism of formation and properties[3-6].

There are two exfoliation types to produce single-layer materials starting from GICs: mechanical and thermal. The thermal exfoliation technique is the fastest process and can produce graphene in gaseous environment. The technique mechanism depends on the heating process, a pressure is exerted in the graphite layers by the gases of the functional group decomposition. When this pressure is bigger than van de Waals interlayer attraction the exfoliation occurs[7].

In this work the $FeCl_3$-H_2SO_4-C was prepared and three types of heat treatment were made. The samples were analyzed by X-ray diffraction, Raman spectroscopy and by scanning electron microscopy. After this, a second heat treatment was made under 2 g (g = 9,809 m/s²).

Gravity can influence the mass and heat transfer, also the convection speed is altered. The gas/liquid flux can be changed by Coriolis acceleration effect, changing the gravitational convection, and solid can be plastic deformed by the weight gain[8]. Process to produce graphene layers using high gravity as a parameter is a reality, but this kind of process is most used in liquids methods[9,10].

2. Experimental

2.1. GBC's production

The $FeCl_3$-H_2SO_4-GIC was prepared with 20g of natural graphite with particle size of 300 µm, 100 ml of H_2SO_4 solution (75%), 7,2g of $KMnO_4$ and 3,4g of $FeCl_3$. After mixed, the GBC was heated to 40°C per 1h. At the end washed with deionized water.

2.2. Heat treatment

The furnace was previous heated in air at temperatures set points: 400 °C, 600 °C and 920 ºC. The samples were put into the furnace for about 10 min, and posteriorly, the samples were cooled at air.

2.3. High gravity experiments

The high gravity experiments were performed at a centrifuge for materials processing [11]. The sample was fixed at middle of furnace, coupled to the centrifuge arm (Fig. 1), in an open quartz ampoule. The experiments were performed with 2 g of acceleration.

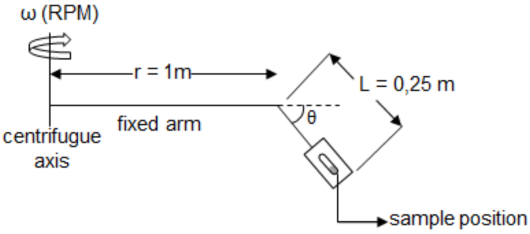

Fig. 1. Centrifuge setup for high gravity experiments.

The furnace was previous heated in air at temperatures set points: 570 °C, and 650 ºC. The heat treatment methodology was show at Fig. 2. Where, samples were heated about 2,5 min with furnace stopped, 5 min under 2 g acceleration and 2,5 min stopped again. The total time of the heat treatment was about 10 min.

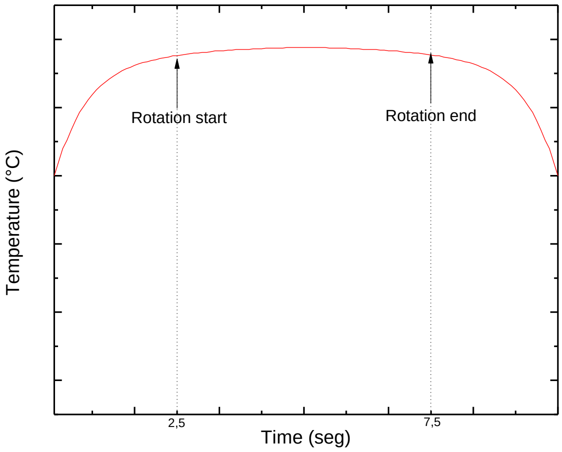

Fig. 2. Experiment temperature profile.

2.4. Characterizations

The microstructure of samples was characterized by scanning electron microscopy (SEM), Tescan Mira3, for structure characterizations was made X-ray diffraction, Philips X'Pert, with Cu $k_{\alpha 1}$ radiation (λ = 1,54Å), the XRD pattern can be used to calculate the crystallinity parameters[12,13], as: the interlayer spacing (d), crystallite height along c-axis (Lc) and crystallite height along a-axis (La). Lastly, was made a Raman spectroscopy, at Renishaw microscope system 200, with 514,5 nm of argon ion laser. Then, from the Raman spectroscopy peaks, it was possible, quantitatively, to evaluate the change in the graphite organization through fitting by the first-order peak D and G using the method of Sadezky and the smallest square-chi[14,15]. This method consists of combination of four Lorentzian bands (G, D1, D2, D4) and a Gaussian band (D3). The D1 and D2 bands has been proposed to originate from surface graphene defects, the D3 band has been attributed to amorphous carbon, and the D4 band has been attributed to polyenes and/or ionic impurities. The G peak is due to the C-C bond stretching of all pairs of sp^2 atoms in both rings and chains.

3. Results and Discussion

In the XRD result (Fig. 3.) it possible see the diffraction patterns of graphite and MnSX compounds with different stoichiometries. The results of crystallinity parameters were present at Tab. 1.t along a-axis (La) (Tab 1).

Tab 1. Crystallinity parameters of GBC samples.

Sample	d (002) nm	Lc (nm)	La (nm)
400 °C	0,33724	106,24717	264,48715
600 °C	0,33596	259,09562	264,30937
920 °C	0,33613	76,956913	180,66763

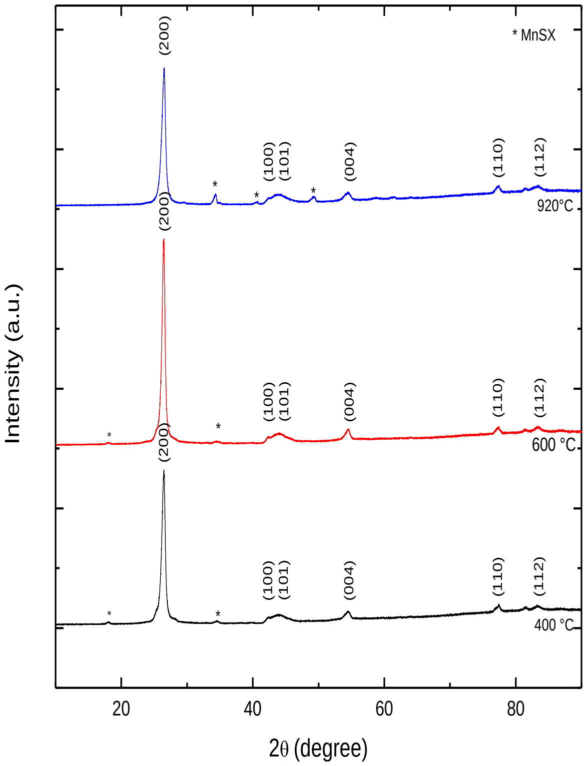

Fig. 3. Graphite samples XRD patterns.

It is possible to see in SEM images (Fig. 4) the non-clear MnSX compound accumulated at boundary of graphite layers. The 300 °C and 600 °C has two intense picks at 17,9579° and 34,4918°, correspondent to $MnSO_4$. H_2O (00-001-0565). The 900 °C sample has three intense picks, the picks in position 34,4399° and 49,43254° may be related to MnS (00-065-2919). However, the composition of this impurity compound stays unclear.

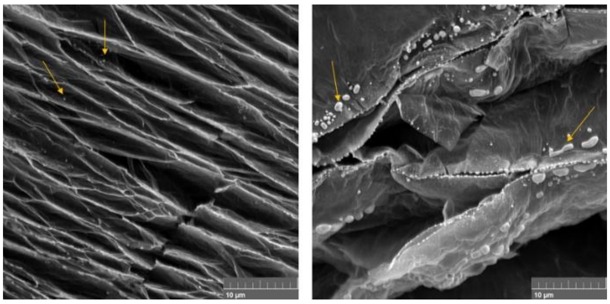

Fig. 4. Impurity compound in graphite layers.

Figure 5. show the Raman spectroscopy of graphite samples for different heat treatments. The sample 400 °C has all bands and the bigger D2 value, including amorphous carbon. Higher temperatures show fewer defects in samples (D1 and D2), the 920 °C sample shows less defect, with tendency to graphene.

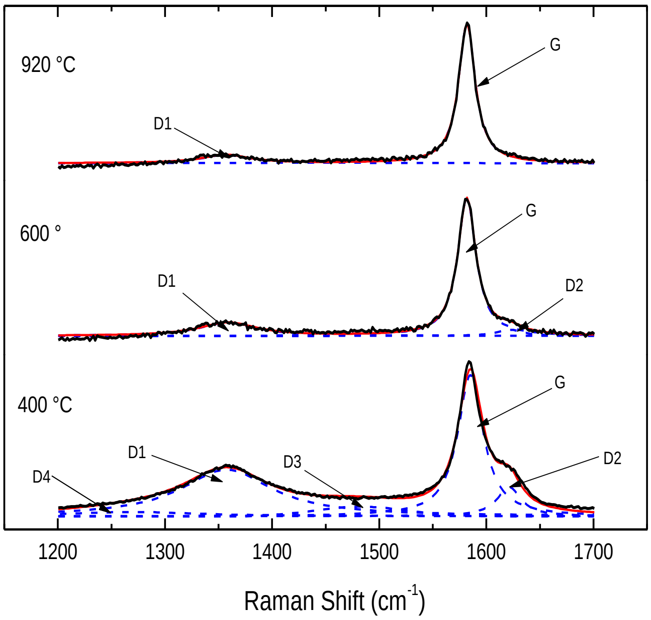

Fig. 5. Raman spectroscopy of graphite samples for different heat treatments

The intermediary temperature was also made in high gravity condition. The XRD pattern of samples processed at 2g shows a significant inclination after plane (100) (Fig. 6). However, Raman spectroscopy analysis does not shows different bands and the D3 band (carbon amorphous band) was not present in these samples. More analysis will need to make for determination of this phenomenon.

The compressive load by gravity during the experiments is very clear in La and Lc crystallinity parameters (Tab 3.). Gravity reduce both crystallite height along axis-a and axis-c.

Tab. 2. Crystallinity parameters of high gravity processed samples.

Sample	d (002) nm	Lc (nm)	La (nm)
600 °C	0,33596	259,09562	264,30937
570 °C	0,33613	76,956913	180,66763
650 °C	0,33742	39,870741	53,58124

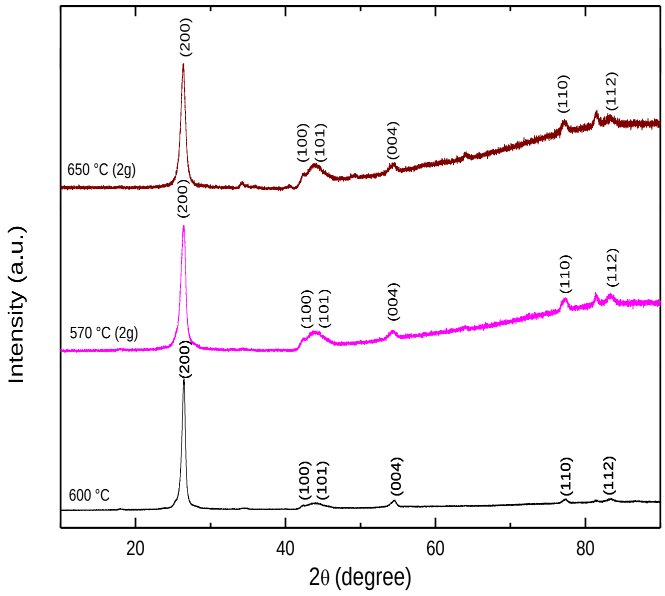

Fig. 6. XRD patterns of samples processed at high gravity

All results show EG formation. The process used did not got exfoliated graphite. We supposed that the time between GIC production and heat treatment may have influenced.

4. Conclusions

Three thermal process was made in a GBC to produce exfoliated graphite. The results indicate the formation of EG, and the best expanded method was used for sample 600 °C, by crystallinity parameters, with few defects, by band combinations.

High gravity influenced directly at crystallinity parameters, reducing the Lc and La. The difference in the XRD pattern of normal gravity and high gravity will be investigated. Once, Raman spectroscopy results, does not corroborate to take a final conclusion.

Acknowledgments

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