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Preparation Methods of Carbon Nanotubes

Edinilson José Slabei[1], Alfredo Bruger Junior[1], Elias da Costa[2], Gino Capobianco[3]

1. Production Engineering – UNIGUAÇU

2. Universidade Estadual do Paraná – UNESPAR

3. UNIGUAÇU

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Abstract: The present work presents the study of the use of carbon nanotubes (CNTs), aiming to improve the mechanical properties of basalt derivatives. In this first stage of the research, the main methods of preparation of CNTs were evaluated, showing the temperatures, the main catalysts used the types of carbon nanotubes, ways to obtain higher quality CNT and higher performance methods. As results, it was possible to report that the methods that stand out are the CVD (chemical vapor deposition), current arc and laser ablation, with CVD being the most used. The results are preliminary and base to report results regarding the application of nanotubes in the improvement of basalt derivatives in future research.

Key words: Carbon Nanotubes, CNT, methods of preparation.

1. Introduction

Carbon nanotubes were observed in 1991 by Sumio Lijima (LIJIMA, 1991) during surface studies of graphite electrodes used in an electric discharge method for fullerene synthesis (ROMERO, 2002). From this and with the intensification of the studies, it was discovered that this material has excellent mechanical, electrical and thermal properties, high surface area, among other properties, curiosities and a huge range of applications (BAUGHMAN et al., 2002; HERRERO, 2004; THOSTENSON et al., 2001).

However, in order to be able to apply on an industrial scale, increasing the quantity and improving the quality of the nanotubes produced, it is still necessary to study and research of new methods of synthesis or

Corresponding author: Alfredo Bruger Junior, Production Engineering – UNIGUAÇU.

improvement of the existing methods, because the questions revolve on how to obtain long fibers, high purity and low cost (DROPPA JUNIOR, 2004).

High temperature (above 3000 °C) methods as well as laser ablation and chemical vapor deposition methods produce high quality structural carbon nanotubes, but their industrial productivity is questionable and the cost of the product is high (LEONARDI, 2014). Moreover, we do not yet have complete control over these processes.

Among the existing methods, those that stand out are the CVD (chemical vapor deposition), current arc and laser ablation. The CVD is the most used, because it does not require high temperatures, it is possible to produce in a cheaper way, it has the possibility to produce long fibers and it is already possible to produce in an industrial scale (BIERDIEL, et al., 2007; PILATOS, Et al., 2016, ZARBIN; OLIVEIRA, 2013).

2. Discovery of Nanotubes and Evolution of Preparation Methods

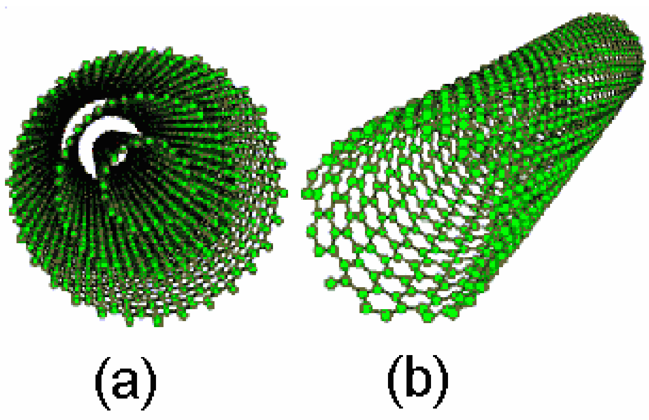
In 1976, Endo and colleagues were probably the first researchers to report the existence of carbon nanotubes (MARTÍNEZ, et al., 2013). Despite this research and others reported in the 1950s, but nothing proved, studies and interests over CNTs were intensified only in 1991 (LIJIMA, 1991), when the Japanese scientist Sumio Iijima obtained multiple wall nanometric carbon fibers, obtained from the arc discharge synthesis. In 1992, Ebbesen and Ajayan conducted the first macroscopic production of CNT, being produced by arc discharge, SWNTs and MWCNTs. In addition, in 1993, CNTs were produced by the chemical vapor deposition (CVD) method (SALES, 2013).

In order to be able to continue the generation of nanotubes and the need for large-scale production, because the researchers quickly thought about several applications, it was necessary to improve and develop new synthesis techniques (DROPPA JUNIOR, 2004), some that need higher temperatures, higher times, more expensive substances and materials, the use of catalysts, submit the nanotubes to the purification processes that in many cases make production expensive, etc., and so we have today with the methods that better serve industrial demand, still need to improve greatly to meet production needs and enable the expansion of CNTs applications.

3. Nanotubes Types

Carbon nanotubes are generated in cylindrical form by means of graphite layers (ROCHA), and can be divided into two groups, single wall carbon nanotubes (SWNTs) and multiple wall carbon nanotubes (MWCNTs) (OLIVEIRA, Et al., 2011, MARTÍNEZ, et al., 2013, ROMERO, 2002). The Carbon nanotubes are generated in cylindrical form by means of graphite layers (ROCHA), and can be divided into two groups, single wall carbon nanotubes (SWNTs) and multiple wall carbon nanotubes (MWCNTS) (OLIVEIRA, Et al., 2011, MARTÍNEZ, et al., 2013, ROMERO, 2002). The SWNTs can be considered as a single sheet of graphene wrapped around itself to form a cylindrical tube, being more difficult to obtain the same, however, they stand out because they have greater stability and better mechanical properties, besides having more possibilities of application. The MWCNTs are formed by two or more layers of concentric atoms, that is, they are formed by 2 or more SWNTs (DAI; MAU and NEMES apud MARTÍNEZ, et al., 2013; LEONARDI, 20014). Below you can see how each structure behaves.

Picture 1: a) Basic structure of a multi-walled nanotube; B) Basic structure of a single wall nanotube (COUTO, 2006).



A certain amount of one or the other is obtained because of the synthesis method used, the temperature, the gas pressure, the geometry of the system, but mainly the use of a catalyst (ROMERO, 2002). But in a way the type of CNT produced will depend and be influenced directly by the type of synthesis used, since each one has possible internal variations that stimulate the generation or not generation of CNTs, as well as its structural differentiation in SWNT and MWCNT.

4. Preparation of Carbon Nanotubes

The methods of preparation of carbon nanotubes differ from each other and according to Sales (2013, p.16):

> Synthetic mechanisms are highly important in that, depending on their choice, they lead to materials with different levels of purity. The goal is to increasingly improve the synthesis processes in order to obtain increasingly pure materials, which in turn will reduce its cost, since all the post-treatments will be decreased.

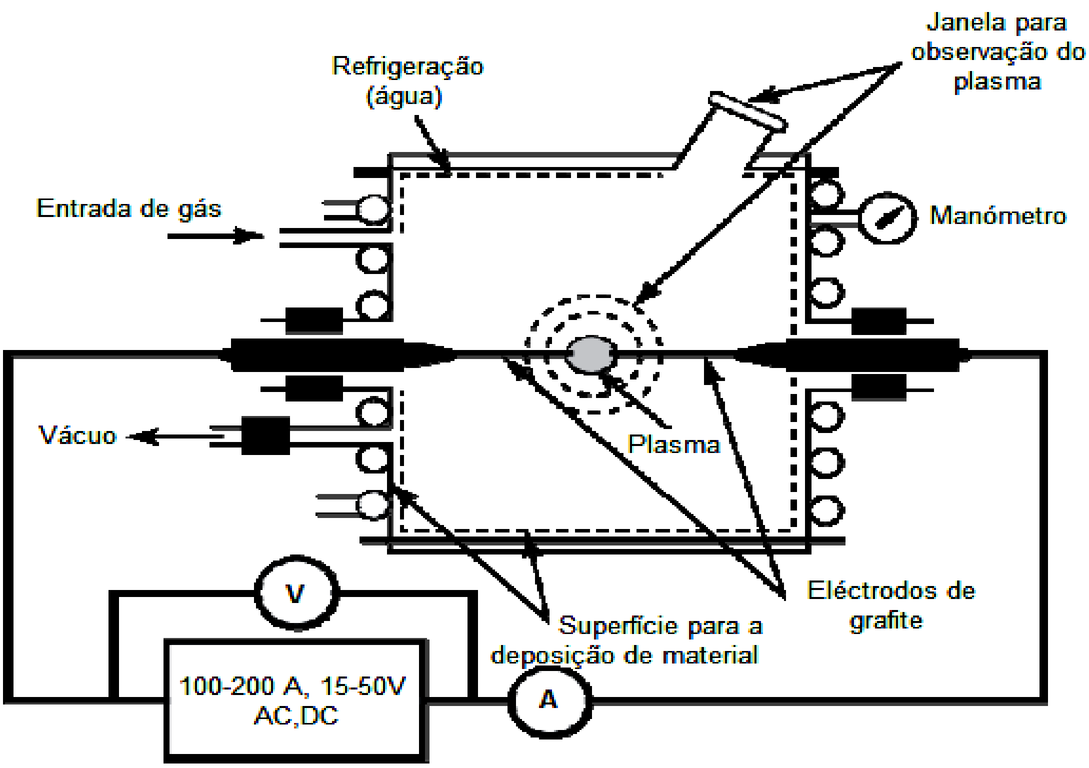
On top of this, it is necessary to improve the preparation of the NTCs and reduce the production costs, so that they are the purest possible, that they have larger structures, with greater resistances and that they have a greater range of application in the medium Industrial (TEIXEIRA, 2010).

Taking into account the methods currently used, CVD as presented, is what has been used the most in the preparation of CNT, but to some extent all add to the development of new synthesis techniques.

4.1 Current ARC Method (Arc Discharge)

The arc and current method was used by Lijima in the discovery of carbon nanotubes. It consists of an electric discharge of two electrodes (anode and cathode) of graphite inside a steel chamber, containing inert gas at high pressure (FEITOSA, 2009; SALES, 2013; TEIXEIRA, 2010; TREVISAM, 2009). With the approach of the two electrodes there is the increase in temperature, which is around 3000º to 4000ºC, and with this, the carbon contained in the electrodes vaporizes by depositing in the form of a black soot on the walls of the chamber and the negative electrode, forming the MWCNTs, but also, fullerenes, amorphous carbon and some graphite sheets (DROPPA JUNIOR, 2004; TEIXEIRA, 2010).

SWNTs can also be produced by this method, simply use a metal catalyst introduced in one of the electrodes. Usually the catalysts used in this and other synthesis methods are Cobalt (Co), Nickel (Ni), Iron (Fe), and alloys containing these metals. The quality of the CNT obtained by electric arc depends on the quantity and quality of the catalyst, the geometry of the system, the pressure, the electric current of the cathode and anode distancing during the process, the nature of the inert gas and the synthesis temperature (DROPPA JUNIOR, 2004; TEIXEIRA, 2010).



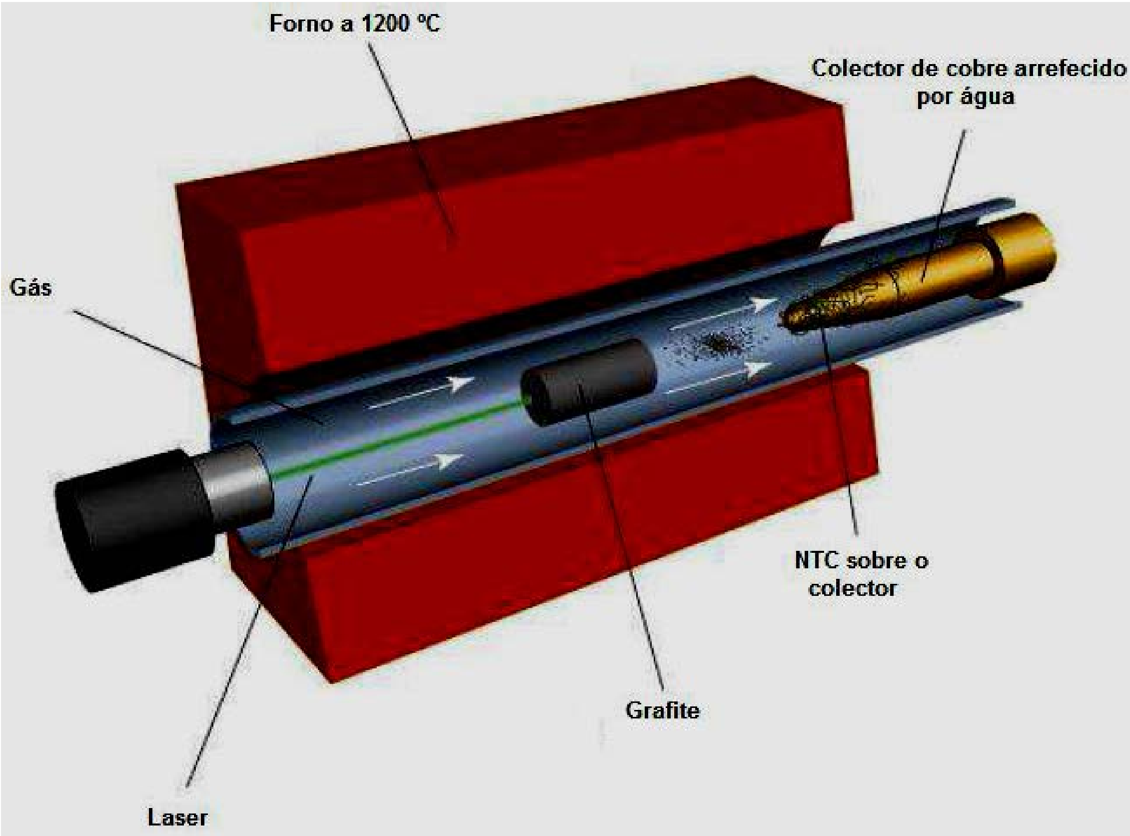
Picture 1: Schematic representation for CNT synthesis by current arc discharge [Journet and Bernier 1998 and Ferreira 2003] apud SALES, 2013, p.17].

The cost of this method is high because it requires graphite electrodes and high purity inert gases. In addition, post-synthesis treatment is necessary for CNT purification, as long as nanotubes are not the only byproducts generated during synthesis (TEIXEIRA, 2010).

4.2 Method by Laser Ablation

This process consists in the evaporation of a graphite billet by the application of a high power laser beam in an inert gas chamber (He or Ar) at a temperature of up to 1200 ° C. With the laser reaching the graphite billet, occurs the evaporation of the carbon, following the gas flow until it is deposited in the copper collector (cooler part of the quartz shell) or in the tube walls (DROPPA JUNIOR, 2004; ROMERO, 2002; SALES, 2013; TEIXEIRA, 2010).

By this method, the SWNTs are generated, and as in the current arc method, this happens only with the use of a metal catalyst. For the production of MWCNTs only graphite billet is enough (DROPPA JUNIOR, 2004; TEIXEIRA, 2010).



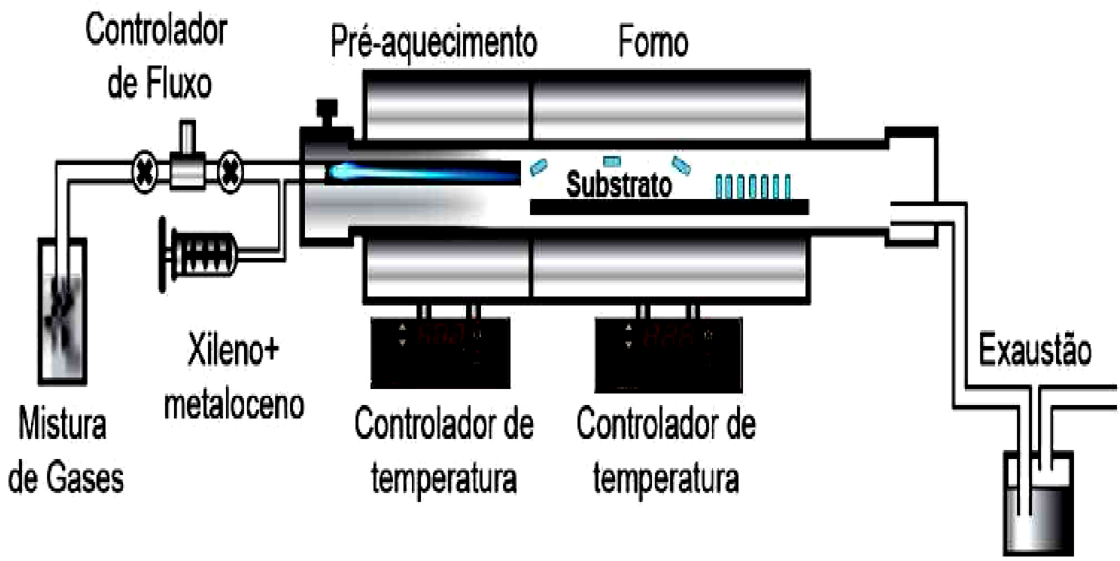
Picture 2: Representation of the procedure through the laser ablation method (Yakobson 1997 and Shibata 2011) apud SALES, 2013, p.19].

Despite the fact that quality CNTs are generated, which contains few impurities and a reduced need for purification processes, it is a costly technique and does not have commercial application of the CNTs produced and that it must undergo a strict temperature control, since in general structures produced below 1200 ° C have many defects and below 200 °C, CNTs are not generated. (DROPPA JUNIOR, 2004; ROMERO, 2002; SALES, 2013; TEIXEIRA, 2010)

4.3 Steam Chemical Deposition Method (CVD)

The CVD (Chemical Vapor Deposition) method enables the production of large-scale carbon nanotubes (ZARBIN; OLIVEIRA, 2013). It consists of the catalytic deposition of the carbon that is generated from a carbon containing gas inside an oven with temperatures of 500 °C to 1100 °C in the presence of a metal catalyst. As in the laser ablation method, CVD also occurs inside a quartz tube (SALES, 2013; TEIXEIRA, 2010; TREVISAM, 2009).

In this synthesis, SWNTs and MWCNTs are generated, by thermal decomposition of the precursor in carbon (solid) that is deposited in a substrate and hydrogen that is eliminated by exhaustion (TEIXEIRA, 2010).



Picture 3: Schematic representation of a chemical vapor deposition reactor [(Andrews et al., 1999 and Ferreira 2003) apud SALES, 2013, p.18].

This technique allows greater control over growth parameters, is used for high yields, as well as, it has less need for purification. With this, the low cost in the preparation stands out, since the purification methods in some cases are extremely expensive. However, this technique can produce nanotubes with structural defects, restricting the application of the CNT generated (SALES, 2013).

5. Metodology

This work is a bibliographical one, which sought to analyze already published materials, through the reading and interpretation of articles, dissertations and others, in order to know in detail the methods of preparing CNTs. Materials were selected for the study of the proposed theme and complementary readings were carried out in other archives in order to answer some questions that arose during the work.

The research was initiated on the discovery of carbon nanotubes, the types of CNTs, the methods used in the first productions, who discovered and how discovered, from this, to know the methods of preparation of carbon nanotubes and study them in detail.

Final Considerations

Today we have the challenge of improving the preparation of CNT. The techniques of current arc, laser ablation and chemical vapor deposition produce high quality nanotubes, but to some extent have their particularities and disadvantages, as seen in the description of each method, and it is necessary to intensify the studies in order to stimulate the advance of this large area.

The focus of this research was to demonstrate how the carbon nanotubes were discovered, to show the types of CNTs, as well as to detail the most used preparation methods. Although it is a quick description of the subject, we realize that we do not yet have an apparatus / method that can produce highly pure nanotubes, at industrial level. However, the research also follows the perspective of analyzing the use of CNTs in the improvement of basalt properties.

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