MINING AND METALLURGY INSTITUTE BOR
and
TEHNICAL FACULTY BOR, UNIVERSITY OF BELGRADE

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53rd International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:
Ana Kostov
Milenko Ljubojev

3 – 5 October 2022. Hotel "Albo" Bor, Serbia

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STRUCTURE AND PROPERTIES OF CARBON NANOTUBES: A REVIEW

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Abstract

Nanotechnology is considered as a key technology of the twenty-first century. The term nanomaterials describes a class of materials with a particle size of 1 to 100 nm. In addition to their size, another specificity of nanomaterials is the large ratio of surface area and volume. Differences in solubility and dispersion in solutions of carbon nanotube depend on their structural characteristics. These are extremely light materials and very strong. They are characterized by the pronounced electrical and thermal properties. Due to their unique physico-chemical properties, such as the high catalytic activity, high physical, chemical and thermal stability, large specific surface area and significant chemical reactivity, they began to be used for the wastewater treatment.

***Keywords**: carbon nanotubes, properties, structure*

1 INTRODUCTION

The simplest division of nanomaterials (NM) is into the inorganic NM and NM based on the organic molecules. Inorganic NMs include the carbon-based NMs (graphene, graphene oxide, carbon nanotubes). While the second group includes the NM, supported by the organic molecules or polymers [1].

Carbon is a chemical element with the atomic number 6. Carbon atoms can bond in different ways to form the structures with completely different properties. They can hybridize in the sp, sp^2 or sp^3 forms. In graphene, the carbon atoms are sp^2 hybridized and dense organized in a proper "honeycomb". This pattern is the basic structure for the other allotropic modifications of carbon, such as the fullerenes and carbon nanotubes (CNTs), which are the sp^2 hybridized. The CNTs were first introduced in 1991, as one of the allotropes of carbon [2].

2 STRUCTURE OF NANOTUBES (CNTs)

The CNTs consist of one or more graphene sheets. Graphene sheets are concentrically rolled to form the tubular structures. Depending on the number of graphene layers, there are the three types of CNT: single-layer (SWCNT), double-layer (DWCNT) and multilayer (MWCNT) [3].

The SWCNT consists of a coiled single layer of graphene. Depending on the wrapping direction of the graphene layer, the three structural types of SWCNT appear. The two predominant types of structural forms of the CNT are "zigzag" and "armchair". The third form of the SWCNT is a chiral and is very similar to a zigzag and an armchair, but it is characteristic that the tube can be twisted in any direction [4,5].

The atomic structure of the SWCNT is characterized by the chirality of the nanotubes defined by the chiral vector $\vec{C}$i with the chiral angle θ. The pair of indices (n, m) describes the chiral vector and directly affects the electrical properties of the nanotubes, and the value of the chiral vector can be calculated using the equation (1) [6].

$$\vec{C}\text{i} = n\vec{a}_1 + m\vec{a}_2 \quad (1)$$

This vector reveals the rolling direction of the graphene sheet, so it is also known as the bending vector. The number of unit cell vectors ($\vec{a}_1$ i $\vec{a}_2$) in the honeycomb crystal structure of graphene along two directions is determined by the integers n and m. The integer pair values determine which form of the SWCNT will occur. When m = 0 (n, 0), nanotubes are called the zigzag nanotubes, when n = m (n, n), nanotubes are called the armchair nanotubes, and the other states (n> m> 0) are called the chiral. The chiral angle determines the extent to which the pipes are twisted. Based on the geometry of the carbon bond around the perimeter of the nanotube, the chiral angle can be 0□ (zigzag) and 30□ (armchair). When n-m > 3 the nanotube is considered "metallic" or highly conductive, and if n-m < 3 the nanotube is a semi metallic or semiconductor. The shape of an armchair is always metal, while the other shapes can make the nanotube a semiconductor [6].

The MWCNTs are composed of several concentric tubes of graphene that are intertwined with each other and held together by the secondary, Van der Waals bond. They appear in two structural forms: the model of a Russian doll and model of a parchment. The model of the Russian doll implies a CNT that contains another nanotube, and the outer nanotube has a larger diameter than the inner nanotube. When a single sheet of graphene is repeatedly wrapped around itself, just like a rolled roll of paper, it is called a parchment model [7].

3 PROPERTIES OF NANOTUBES (CNTs)

The CNTs have nanometer-sized radii (less than 100 nm) but micrometer lengths (greater than 20 μm), which should provide a length-to-diameter ratio > 1000. For SWCNTs, diameters can be 0.4 to 3 nm, and their length is in the range of micrometers. The MWCNTs are constructed of several to several tens concentric cylinders wrapped around a central cavity, with a regular periodic spacing of 0.34 to 0.39 nm. The interlayer distance in the MWCNT is approximately the same as a distance between the graphene layers in graphite, however the CNTs are several percent bigger than the graphite crystals. The inner diameter value of the MWCNT varies depending on the number of layers and ranges from 0.4 nm to several nanometers, and the outer diameter from 2 nm to 30 nm. The ends of the MWCNT are usually closed by dome-shaped semi-fullerene molecules (pentagonal ring defect), whose role is to help to close the tube at both ends [7,8].

3.1 Mechanical properties

Due to their low density, the nanotubes have excellent mechanical properties. The existence of sp^2 bonds between carbon atoms in the CNT makes them one of the strongest materials in the world. This bond is even stronger than the sp^3 bond found in diamond. The multilayer nature, in the outer walls of the MWCNT, protect the inner nanotubes from a chemical interaction with the external substances, and provide a high tensile strength. It is thought that the SWCNTs can have a tensile strength a hundred times stronger than steel. The CNTs are said to be very rigid materials, with a tensile strength of about 10–100 GPa.

Defects in the structure of nanotubes, such as the defects in atomic voids, can weaken the strength of nanotubes. A group of scientists used an atomic force microscope (AFM) to investigate what happens inside a nanotube when it is exposed to the high tensile loads. In the MWCNT, the farthest tube fails first, followed by further sliding of the nanotubes within the bundle. This type of tensile load defect is called the "sword and mantle" [9].

Another mechanical property of the CNTs is elasticity. The Young's modulus of elasticity is actually an indicator of material stiffness, and it has a high value for the CNTs. For the SWCNT, it is 1.25 TPa (which is 5 times larger than steel), and for the MWCNT 1.8

TPa. It was found that the value of the Young's modulus is affected by a pipe radius and decreases with increasing number of layers in the MWCNT structure. The obtained module values varied from 4.70 to 1.04 for the number of layers from N = 1 to ∞. Under the great force and pressure, they can bend and twist without damaging the nanotubes, but the nanotubes will return to their original structure. Their bending is also possible at large angles, up to 110°. The properties are the same for all nanotubes with a diameter greater than 1 nm. Chirality has a relatively small effect on the elastic properties of CNTs [10].

3.2 Electrical and thermal properties

Unlike metals that conduct heat by moving the electrons, the CNTs (like diamonds) conduct heat by vibrating the covalent bonds that hold carbon atoms together, the atoms themselves move around an imaginary axis and transfer heat through the material. The thermal conductivity of the CNT at room temperature is very high (<3000 W/mK), and is said that exceed the values of the most well-known heat conductors including diamond. Figure 1 shows a graphical representation of the values of thermal conductivity divided by temperature, K/T, for the SWCNT of different dimensions. All four SWCNT samples show a linear K (T) at low temperature, as shown by a constant K/T value. The results indicate that for samples with a diameter of 1.4 nm, K/T begins to increase to approximately 35 K (K/T value is normalized to 1 for all samples), while a similar increase is not observed on samples from 1.2 nm to approximately 40 K. It can be concluded that the conductivity values are higher for longer than for short samples.

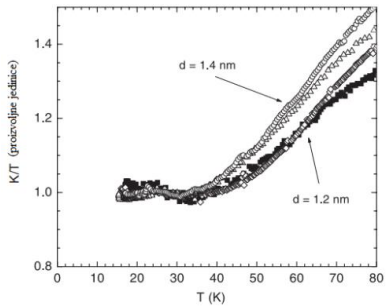

Figure 1 *Thermal conductivity of the SWCNT of different dimensions at different temperatures [11]*

As the temperature increases, so does the value of thermal conductivity. On the other hand, increase in defects in the nanotube (vacancy defect and conformation defect) causes a decrease in thermal conductivity [11].

The electrical properties of the SWCNT can be described as metallic or semiconductor, depending on a direction of twisting of a graphene plate. The SWCNT with the structural shape of an armchair have electrical properties like metal. Only about a third of zigzag and chiral nanotubes have electrical properties like metals, while the other two thirds have electrical properties like semiconductors.

The reason why the CNTs conduct electricity better than metal is in fact that when electrons are transferred through metal, there is a certain resistance to their movement. Resistance occurs when electrons collide with the metal atoms. When an electron is transferred through a nanotube, it travels according to the rules of quantum mechanics. It behaves like a wave that travels through a smooth channel without atoms that it can encounter. This type of quantum electron motion within nanotubes is called a ballistic transport.

However, there are factors that can interfere with the electrical performance of the CNT. Structural defects created during the synthesis process can disrupt electron transfer in the CNT. The CNTs have very high electrical and thermal conductivity, current carrying capacity, combined with very low weight, which makes them perfect electrical conductors [12].

4 CONCLUSION

The CNTs offer numerous advantages over other materials because they possess a unique structure as well as the mechanical, thermal and electrical properties. They consist of hybridized carbon atoms of a hexagonal arrangement and, by wrapping, one sheet of the graphene SWCNT is formed, and several sheets of graphene form the MWCNT. They have high values of modulus of elasticity and tensile strength. Both structural forms are characterized by the metallic or semiconductor electrical properties, while with a thermal conductivity of 3000 W/mK at room temperature, it exceeds the values of the most well-known heat conductors.

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