Growth And Agglomeration Of Carbon Materials Under Microgravity Conditions

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ABSTRACT

The PCPM (Unité de Physico-Chimie et de Physique des Matériaux de l'UCL) research activity in relation with the 1994-2000 microgravity programme is presented within the more general frame of the work which has been undertaken in the laboratory since the early eighties on carbon materials. In this context, a group of PCPM researchers has essentially focused on two research areas in which they have been heavily involved these last twenty years: carbon materials and polymer-matrix composites. Concerning carbon materials, the aim is to understand the growth mechanisms by studying the carbon plasma generated between two graphite electrodes under microgravity. Various forms of carbons, including diamond, have been so far investigated. As to the contribution to the study of composites, the effect of microgravity on the mechanisms of carbon black agglomeration in a fluid is investigated.
As regards to the organization of the paper, a relatively detailed introduction describing the properties of carbon materials, with particular emphasis placed on their recently discovered forms, such as fullerenes and carbon nanotubes, is first presented. The various contributions of our team to the subject are also included. Then, after describing the experimental setup, the research performed under microgravity conditions is presented and the results obtained discussed.

INTRODUCTION

The PCPM activities in the microgravity programme have essentially focused on two research areas in which part of its researchers are heavily involved since the early eighties: carbon materials and polymer-matrix composites. The aim is to study the carbon plasma generated between two graphite electrodes under microgravity conditions and to investigate the effect of microgravity on the mechanisms of carbon black agglomeration in composites. After introducing the state of the art (§2.1), including the PCPM contribution to the subject (§2.2), we will first discuss in section 2 our activity related to carbon growth between the graphite electrodes in general (§2.2.1), then turn to the specific case of diamond (§2.2.2). We will then present the research we have carried out under microgravity conditions (§2.3) and discuss briefly the provisional results (§2.3.2), after describing the experimental setup (§2.3.1). In section 3 we will present our work in relation with the agglomeration of carbon particles under microgravity conditions (§3). Finally, in Appendix I, we give a brief outlook of the PCPM laboratory, and, in Appendix II we present a selection of papers related to carbon materials and their composites published by the team.

CARBONS AND GRAPHITE

State of the Art

General

Carbon is one of the most versatile chemical elements, which forms the backbone of almost all molecules important to life, such as DNA, proteins and oils. The unique character of carbon stems from the ability of its atoms to form stable bonds among themselves, while most other elements prefer different partners in chemical bonds. Since the late eighties, there were only two known forms of pure crystalline carbon: diamond and graphite. In diamond every carbon atom has four connections and in graphite the number drops to three. In diamond every atom is surrounded by four other carbons, forming a three-dimensional network (Fig.1.a), whereas in graphite every carbon binds with three neighboring atoms in a plane, leading to a chicken-wire like sheet (Fig.1.b). These graphitic sheets are loosely coupled with one another and slide easily, giving it a soft texture. If only two connections were allowed, a chain of carbon atoms would result (Fig.1.c).

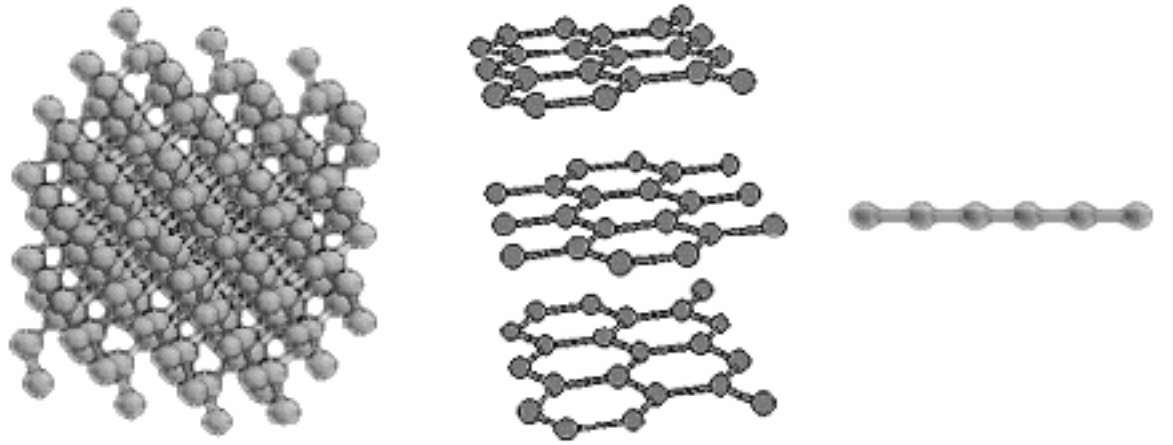


Figure 1: a) diamond b) graphite c) carbon chain

In addition to bulk graphite and diamond, carbon materials are found in a variety of forms such as carbon black of various origins, carbon fibers, fullerenes and carbon nanotubes. These two last forms, which have been discovered recently, will be discussed in the next section (§2.1.2). These various forms of carbon may be quite different with regard to structure and properties.

Carbon fibers and carbon black are widely used in industry as fillers to improve the mechanical, electrical and optical properties of the matrix in which they are dispersed, for example as reinforcement in tires [1-2].

The diamond structure (3-dimensional) is probably the most thoroughly investigated among all crystallographic structures. The extreme hardness is used for industrial tools.

The fullerenes (0-dimensional) and carbon nanotubes (1 or 2 - dimensional) are an interesting class of nanostructures [3-5]. These carbon forms are generally in the range of

1-25 nanometers in diameter and many microns in length for nanotubes and, hence, they can fit well into submicrometer- scale components approaching the limit of miniaturization in newly emerging nano-technologies and electronic devices. Another area, which attracts interest, is the idea of using these particles as ‘molecular containers' with possible applications in catalysis or as biological sensors.

Fullerenes and Nanotubes

Two branches of chemistry emerging in the 1970's, astrophysical chemistry and cluster science, opened the way for some exciting discoveries with the help of Radioastronomy. Radiosignals generated by vast clouds of millions of tons of gas in interstellar space could be used to detect molecules. Researchers also found strange molecules that had not been synthesized in the laboratory! Meanwhile, back on earth new methods of generating and detecting aggregates of atoms in the laboratory that stuck together in novel ways led to a new class of molecules called clusters. Typically clusters are in a transition zone between molecules and solids and their properties reflect this strongly. Chains and other aggregates of carbon atoms can be considered as clusters. In 1985, Kroto and Smalley collaborated on a project to simulate conditions of such red giant stars in the laboratory. In Smalley's machine, a powerful laser evaporated a piece of graphite into a hot cloud of particles that were cooled with a stream of helium gas, allowing atoms to condense into clusters. The mixture was analyzed by means of a very sensitive mass-spectrometer, which indicated a large number of molecules with a mass of 720. The only elements present were helium and carbon. Since helium is a totally inert gas, the conclusion was that the large molecules must be made of 60 carbon atoms (Fig.2.a), each of which has a mass of 12.

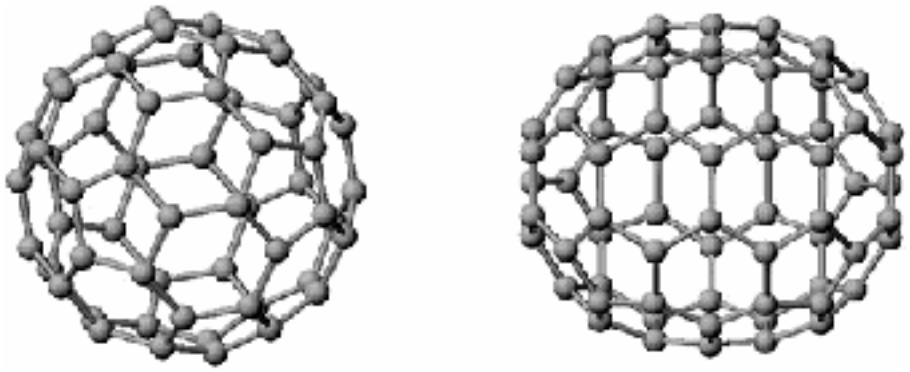
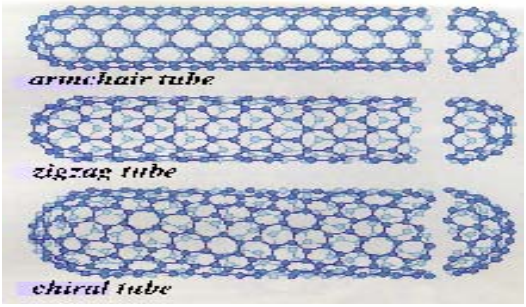


Figure 2: a) C60 molecule b) C70 molecule

The 60 carbon atoms are organized to look like a football (Fig.2.a). Due to its structural symmetry, which featured prominently at the time in some constructions of the architect Buckminster Fuller, the scientists named the molecule buckminsterfullerene. Buckminsterfullerene is often shortened to fullerene or buckyball. Very quickly, large quantities of C60 were about to be synthesized using the arc-discharge method. But it soon turned out that there were other cage structures to be found in the soot, like C70, which looks a bit like a rugby-ball (Fig.2.b).

Fullerenes have stimulated intense and diverse activity in the physical sciences community, in particular leading to the discovery of a host of carbon-based materials with particular nanoscale shapes and forms. This new research field is turning out to be an innovative branch of materials science at the interface between molecular and bulk systems.

When the arc power supply was changed to direct current instead of alternating current, strange tubular structures were found in one of the electrode's deposits. These tubes are entirely made out of carbon and were named nanotubes, referring to their diameters, which are only a few nanometers wide. They were first observed and reported in 1991 by a



Figure

One can also introduce "defects" into the straight tube, which is made up from carbon atoms binding exclusively in hexagon patterns by reducing or adding one carbon bond. The resulting pentagons and heptagons can introduce kinks, curvature and the like. So it is possible to create nano-spirals (Fig.4), nano-doughnuts, capped-ends on tubes which have all been observed.

These nanotubes are incredibly strong - several hundred times stronger than steel, partly because of the hexagonal geometry, which can distribute forces and deformations widely and partly because of the strength of the carbon-carbon bond. As mentioned above, they have unusual electronic properties. Already simple electronic devices, such as diodes, switches and transistors have been realized using nanotubes, which are much smaller than their silicon equivalents used in today's computer chips. Research is under way to produce carbon nanotubes reliably and under defined conditions. When such methods have been found, nanotubes will appear in electronic devices and also in new, super strong materials.

Japanese scientist, Sumio Iijima. A straight single-walled nanotube can be made by rolling a flat graphitic sheet into a cylinder. This can be done in various ways, resulting in different kind of nanotubes (called "armchair", "zigzag" and "chiral")(Fig.3). Depending on the exact arrangement they exhibit different electronic properties, some are predicted to be metallic while others are semiconductors.

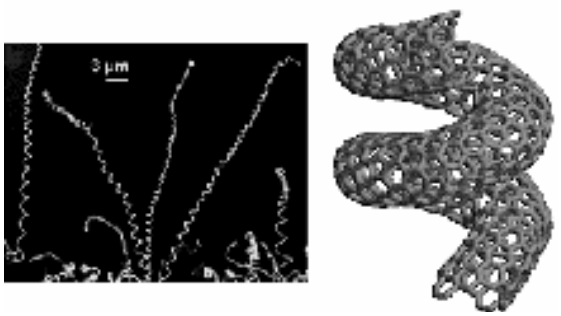


Figure 4: Spiraling carbon

Carbon Materials at PCPM

General Outlook

Since the late seventies our laboratory has been heavily involved in experimental research programmes on the thermal and electrical properties of carbon materials, including polymer matrices filled with carbon fibers or carbon black. Many forms of carbons and graphites have been studied, including their intercalation compounds [6-7]. At present, research efforts are mainly directed on carbon nanostructrures like fullerenes and nanotubes. We have been using *ab initio* calculation and simulation techniques [8], as well as electrical resistivity and specific heat measurements, in order to identify their unique properties.

Different production methods have been used to synthesize these nanoscale graphitic species like electric arc discharge, laser ablation and catalytic decomposition of

hydrocarbons. However the carbon arc is the more convenient way to generate these particles because of the high temperature of the plasma, which may reach 3700 °C. When the arc-discharge is carried on by keeping the gap between the carbon electrodes at about 1-2 mm, cylindrical deposits form on the surface of the cathode. The diameter of this cathode deposit is the same as that of the anode stick. The typical conditions are : with a diameter of the anode carbon of 6 mm, the electric arc current (DC) ranges between 50 A and 200 A (for a voltage of about 20-30 V) and the He pressure in the chamber is in the range 300 - 800 Torr.
This method is based on a simple principle but the formation of fullerenes, nanotubes and recently diamond [9] in this chaotic high-temperature plasma of carbon arc seems an almost magical process which remains poorly understood. Numerous experimental and theoretical studies of the arc discharges [10-11] have shown that the main physical parameters of the space region of an arc next to the cathode surface where the nanotubes are created are: the space and time distribution of density, velocity, and temperature of carbon vapors, electric charge, potential and electrical field. Minor modifications of the synthesis conditions influence all these physical parameters.

Diamond Synthesis

Artificial diamond synthesis was first announced in 1955 [12]. The process involved the presence of a molten transition metal solvent-catalyst at high pressure. Since diamond is the most dense carbon phase, initial approaches used high-pressure techniques to create diamond crystals from carbon. Under these conditions, diamond is the thermodynamically stable phase. However, diamond may also be grown at low pressure as a metastable phase of carbon [13]. This is made possible because of the large activation energy barrier between diamond and other carbon forms. Under appropriate conditions, the kinetics of formation of competing carbon phases can be reduced, so that diamond may grow. Along these lines, pioneering successful results on vapour-grown diamonds were independently reported in the early sixties [14]. Since then, various vapour-grown diamond production methods have been proposed, which have led to higher growth rates and improved sample quality. Nowadays, vapour-phase synthesis of diamond is still a very active area of research worldwide. Synthetic diamond has potential applications in many technological domains of materials science such as abrasives, tool coatings, bearing surfaces, microelectronics (high-temperature active micro-devices, heat sinks, …), optics (laser and X-ray windows), and corrosion protection.
Growing metastable diamond from the vapour phase can be realized by chemical (CVD) and physical (PVD) vapour deposition processes. The PVD process is a synthesis method where the crystallization medium and the resulting crystal have the same chemical composition. Namely, a solid phase of carbon is used as the carbon source for the diamond formation. By contrast, during the crystallization, the CVD process involves the control of the vapour composition. In practice, the essential difference between the PVD and CVD processes lies in this gas activation (hydrocarbon gases), within a hot filament, high-frequency plasma, direct-current plasma-assisted or laser vaporization, or direct low energy ion beam deposition techniques [13-14]. However, all these vapour-phase PVD and CVD techniques suffer from extremely low growth rates (not greater than 100μm per hour for polycrystalline diamond films [13]). To the best of

our knowledge, the PVD process is inadequate for the production of large quantities of diamond micro-crystals.

At PCPM, high-purity diamond micro-particles have recently been synthesized by means of a non-equilibrium physical process [9]. The latter is based on the high-rate nucleation and growth of diamond in the dense carbon vapour generated by a fast and intense heat pulse. The carbon plasma was formed in a stainless steel vacuum-tight chamber by an electric pulse discharge (~1000A, ~10-100ms) between two sharpened tips of high purity (99.999%) graphitic electrodes (Fig.5). The pulsed current was generated by an electric capacitor (0.5 F) charged initially to 30V. In order to remove the gaseous impurities prior to the pulse generation, the chamber was filled with helium, which was then pumped out. This procedure was repeated several times, while a continuous heat treatment of the carbon electrodes at 600-800K was maintained by means of an electrical current.

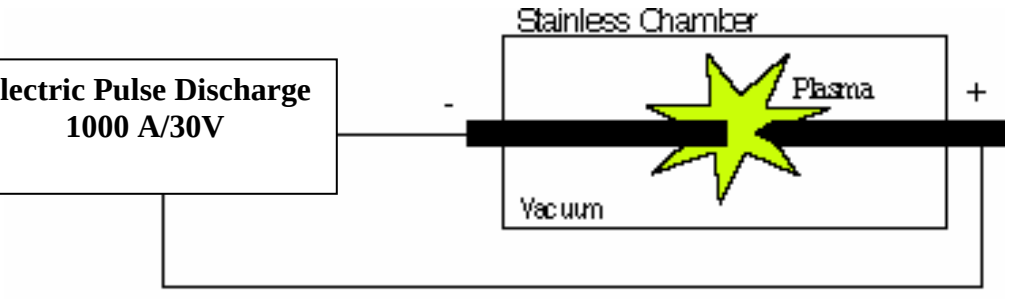
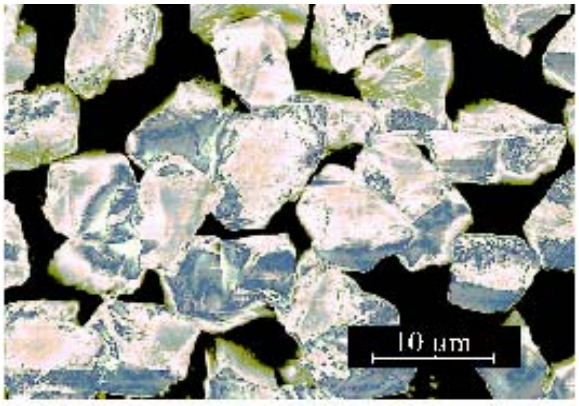


Figure 5: Experimental setup for diamond

The dynamic pumping down to 0.01-0.05 Torr was carried out, through low temperature (77K) adsorption and standard room temperature filters connected in series. A set of different substrates, such as nickel, silicon, aluminum, and quartz, in the form of 10 cm^2 - plates, were used for the sample deposition, and were located at a distance of 5 to 10 mm from the carbon electrode tips, in the region of high carbon concentration. During the electric discharge, the substrate was maintained at room temperature.

At the end of the process, hundreds of brilliant colorless particles (~10μm in size) were detected on the substrate by an optical polarization microscope (Fig.6). Some larger particles, reaching nearly 100μm have also frequently been observed. The average density of particles on the substrate surface (~10cm^2) was determined to be within the range of 10-50 micro-particles per cm^2.

However, the micro-particles were not distributed randomly, but instead were assembled into dense clusters at various locations of the substrates. The size and the density of these micro-particles were found to be independent of the nature of the various substrates used. The mean rate for diamond



growth was estimated to exceed 100 μm/s.

Figure 6: Scanning electron micrographs of diamond microparticles synthesized by arc-discharge

Several identical discharges were performed, with the substrate located further away (50-100 mm) from the graphitic electrode tips. The average size of the diamond micro-particles produced remained around 10μm. This surprising result suggests that the diamond particles form in the high concentration carbon vapour phase, and not at the substrate surface, which is the case in usual chemical or physical deposition processes. When the dense carbon vapour phase is no longer sustained, the completely formed diamond micro-particles drop on the substrate, explaining the random stacking observed in the previous Figure. In such a synthetic process, the diamond micro-particles are probably electrostatically charged, explaining the observed self-assembly in clusters.

Effect of Gravity on a Carbon Plasma Created by the Arc Discharge Technique

Experimental Set-up and Procedure

The objective of our experiment, which boarded the 26th and 28th ESA parabolic flight campaigns, is to carry out a spectroscopic analysis of a carbon arc plasma under varying gravity conditions, to detect any possible influence of the gravity on the plasma properties, especially its geometric spatial distribution (cfr. the dramatic change of a candle flame subject to gravity condition). The plasma is obtained by producing an electrical arc discharge under a helium atmosphere. A high speed spectrometer captures an emission spectrum, from 200 nm to 1100 nm, every 2 seconds. Spectral measurements provide a means to access local plasma temperatures and compositions through the analysis of specific emission peaks.
The block diagram of the experiment is presented in Fig.7 and a view of the system in Fig.8. We used a stainless steel vacuum chamber equipped with:

- two motorized flanges to support the carbon electrodes through insulated copper fingers. The electrodes are connected to a sturdy DC power supply (Hewlett-Packard, 2 kW; max 60A and 35V). The diameter of the electrodes has been machined down to 4 mm.
- appropriate flanges for vacuum and atmosphere control. Helium is used at a pressure ranging from 600 to 800 mbar; vacuum is obtained by membrane pumping;
- plexiglass windows for camera viewing and lighting. A video camera is connected on one LCD screen for direct viewing of the electrodes (for position monitoring);

- UV transparent silica window for the capture of the spectrum;
- a focalization device, composed of a 0.5 mm hole positioned at a 5 cm distance (adjustable) from the spectrometer input optic fiber. The plasma area whose light is captured is estimated to be of 0.25 mm^2. The focalization device is mounted on a motorized stage with the aim of scanning the whole plasma area. The Mechelle 900 spectrometer (from MultiChannel Instruments A.B.) was selected because of its high speed, and the absence of any moving or mechanical part, as are usually found in other spectrometers.

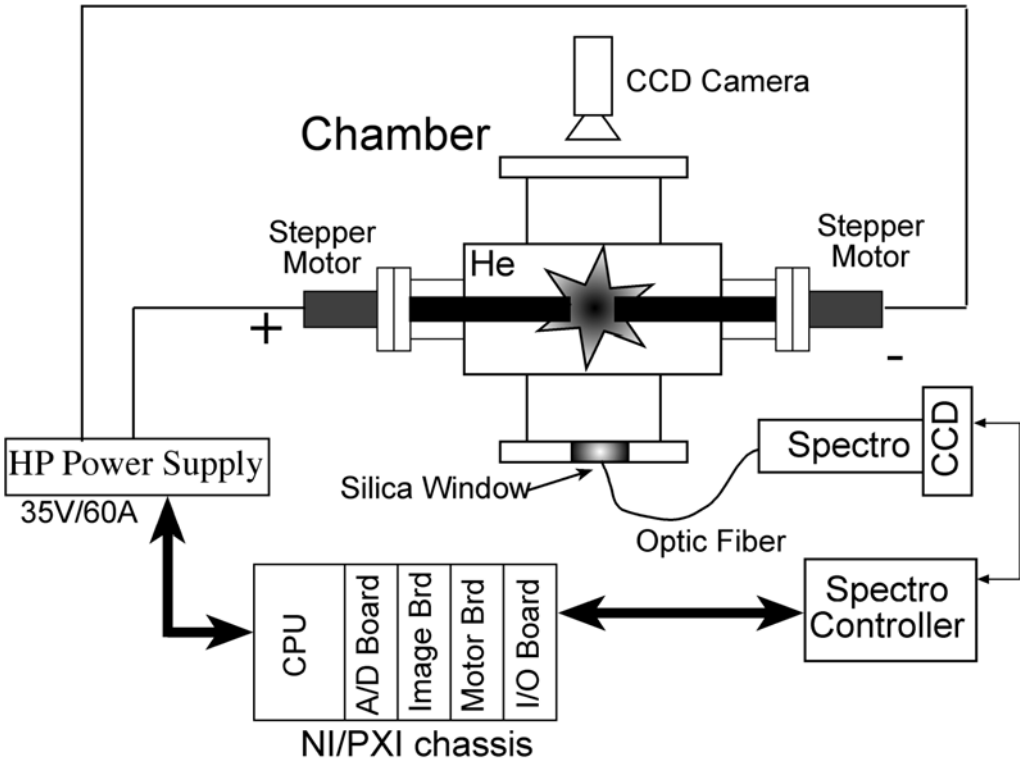
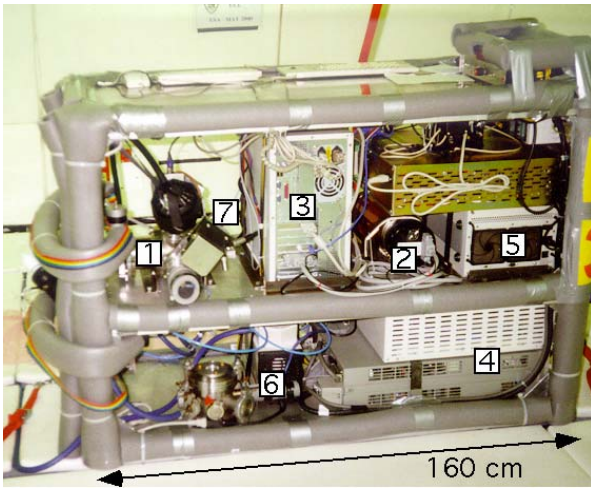


Figure 7: Block diagram of the experiment.



1. Chamber
2. Spectrometer Mechelle 900
3. Spectro Controller
4. Power Supply (HP)
5. NI/ PXI chassis
6. Pump
7. Stepper Motors

Figure 8: View of the system

Our experiment has been designed such as to minimize manual operation. Indeed, the 20 seconds of microgravity available during each parabola, preceeded and followed by hyper-gravity periods, do not provide enough time to control all the experimental parameters. A computer (National Instruments PXI chassis) is equipped with the following interface cards:

- A/D and D/A converters
- digital I/O channels
- stepper motors position control
- IEEE 488 interface (for power supply control)

The three stepper motors (two for electrode movement and one for spectrum capture) and the power supply are controlled by the computer. The gravitometer (supplied in the A-300) is also read in real time.

The computer software has been designed under National Instruments LabWindow/CVI environment, to automate all the experimental procedures:

- at a pre-defined period before the micro-gravity phase, the operator starts an experimental cycle;
- an adjustable delay enables the arc to be initiated under hyper or microgravity conditions;
- after the delay period, the electrodes are brought into contact by the stepper motors. Contact is detected when a current flows through the circuit;
- the motion of the electrode is maintained for a very short (and adjustable) time in order to provide for a sufficiently good electrical contact;
- the spectrometer starts its acquisition;
- after a pre-defined (and adjustable) contact period, the electrodes are “pulled back” and the arc is initiated. The speed of separation as well as the final distance of separation is software adjustable.

PROVISIONAL RESULTS

The first goal of our microgravity experiment is to investigate the effect of gravity variations on the properties (temperature distribution, density, stability,...) of the plasma using spectroscopic methods. This plasma is a mixture of neutral helium atoms, singly ionized carbon ions and molecules, and neutral carbon species. The emission of the (0-0) band of Swan of the C2 molecule can be used to determine the temperature profile near the anode [15-16].

During the 26th campaign, the experimental set-up was designed and mounted without spectrometer, which was only fitted for the 28th campaign. However, the outcome of the 28th campaign was not yet conclusive and the following points should be taken into account in the near future:

- in order to provide "clean and new" surface conditions for plasma initiation, we used a large circular cathode which was rotated in-between experiments to offer a clean surface for each discharge. It seems that this configuration substantially decreases plasma stability. A number of discharges were therefore unsuccessful. We therefore plan to revert to the original small diameter cathode, with a mechanical cleaning process in between the discharges.
- during the hyper-gravity phase, strong vibrations are generated in the plane and, due to the relatively important length of the carbon electrodes and their copper support fingers, they do oscillate, which sometimes lead to plasma interruption. As a remedy, we will install in the chamber a ceramic insulator as a support for the carbon electrodes around the discharge area, which will help maintain their stable relative position during hyper-gravity phases.
- during the plasma discharge, the anode gets eroded while a deposit forms at the cathode. This phenomena shifts the plasma position at such a rate that, within the time of a single parabola, the area analysed by the spectrometer has scanned a great part of the plasma. We need to develop a regulation system to maintain the plasma in a precisely fixed geometrical position.

Artificial diamonds have also been produced under microgravity during the 28th ESA campaign of parabolic flights (Fig.9). The same technique based on the thermal activation of graphite by the arc discharge technique was used to synthesize diamond. Scanning electron micrographs of these particles are shown below. The shape of the diamond particles is more squared than for the ones produced on earth; and they are found to be more isolated on the substrate (no clustering). These experimental observations are however only preliminary results; the diamond particles produced under microgravity are still under quantitative characterization.

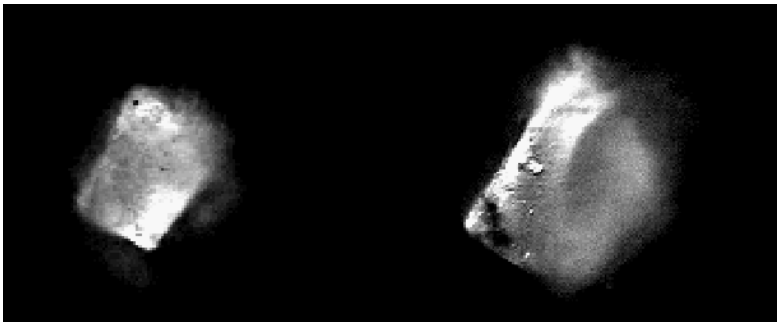


Figure 9: diamond particles produced under

AGGLOMERATION OF CARBON BLACK UNDER MICROGRAVITY CONDITIONS

It is well-known that carbon black is one of the most widely used filler for applications concerning tires. The reinforcement of rubber is directly related to the network structure of the carbon black aggregates in the matrix. For this kind of application, roughly 15 different types of carbon black are available with different surface areas and structures.

Carbon black consists of particles almost exclusively formed of carbon atoms. They are produced at very high temperatures by a wide variety of processes leading to many different morphologies. Among those, the simplest might be represented by spheres with diameters of about 10 nm. The formation of carbon black aggregates in fluids can be modeled, as a first approximation, by either the coagulation or the flocculation theory for colloids.

There are some models which tentatively describe the aggregate size and shape of carbon black, but an accurate measurement of their morphology is difficult to perform. For example, pictures obtained by SEM only show the two-dimensional arrangement of aggregates. Therefore, some techniques, like ultrafiltration and sedimentation are generally used, but their major drawback is that the model (Lorentz-Mie model) assumes that the behavior of carbon black particles in a liquid are like that of spheres, which is certainly not the case. Even using some correcting factors taking into account the fluid drag around an aggregate during sedimentation, the final results remain accidental. Another promising method called PCS (Photon Correlation Spectroscopy) is using the brownian motion of the aggregates. But here again, we are facing sedimentation and agglomeration problems, which affect the calculation of the aggregate size distribution.

Some elementary optical tests like measurements of absorbance may help evaluate the stability of aggregates of various kinds of carbon black in a liquid medium, without the noise resulting from uncontrolled sedimentation due to the gravity. Finally, changes in absorbance are also related to the surface activity of carbon black, which is of primary importance to understand the interaction between rubber and carbon black.

Since at the time of measurement optical techniques were not available on board during the 20^{th} campaign, in exploratory measurements we performed some electrical measurements on the (liquid-matrix) composite. Under microgravity conditions a significant variation of electrical resistivity was observed. However, in these preliminary investigations, it was not possible to conclude whether the effects observed were genuine or artefacts. Optical measurements coupled with electrical resistivity measurements will be performed in a future parabolic flight to get a more complete picture of the situation. The purpose of the experiment is to analyse the changes in absorbance in microgravity of various carbon black types in a solution of chloroform for various carbon black concentrations. Chloroform is the most appropriate liquid for this kind of experiment because of its refractive index. The changes in optical properties, combined with the well known physico-chemical properties, will then be related to the surface activity and to the size of the carbon black aggregates.

CONCLUSIONS

After introducing the state of the art related to various forms of carbon materials including the newly discovered ones, we have presented the PCPM contribution to the subject placing emphasis on our activity related to carbon growth between the graphite electrodes and, more specifically, to the case of a new process of diamond production. We have then outlined the PCPM activity in the microgravity programme which has essentially focused on two specific research topics :

- the study of a carbon plasma generated between two graphite electrodes under microgravity conditions,
- the effect of microgravity on the mechanisms of carbon black agglomeration in composites.

We have briefly discussed the provisional results. It is worth noting that the major part of our activity on the ground consisted in designing and building the experimental arrangements and adapting them to the particular situation encountered on board under microgravity conditions. On board, an important part of the time was devoted to test the mounted systems under these conditions.

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APPENDIX I: An outlook at the PCPM laboratory

Physico-Chemical and Physics of Materials Laboratory (PCPM)

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RESEARCH OBJECTIVES

The research effort at PCPM is aimed at understanding the basic properties of advanced materials in view of finding potential applications and contributing to the development of industrial products. The basic aspect consists in probing the microscopic properties of solids at the atomic and the microstructure scales, using various experimental and theoretical tools, to correlate them when possible to the macroscopic behaviour.

A Brief Outlook at Research Programmes

The team of PCPM -roughly 40 people- is involved in three main research areas:

- electrical, thermal and magnetic properties of solids and their practical applications with particular emphasis placed on the transport properties of nanoscopic systems at low and ultralow temperature.. The temperature region investigated covers the liquid helium range (0.01 to 4.2 K) up to about 500 K and samples of submicronic sizes are commonly investigated. The properties include electrical and thermal conductivities, thermoelectric effects, galvanomagnetic and thermomagnetic effects, superconductivity, specific heat and thermal expansion, magnetic susceptibility,... The materials studied are semimetals, intermetallic compounds, diamond, graphite and its intercalation compounds, carbon fibers, polymers and composites, high Tc superconductors and other electrical ceramics, magnetic multilayers, GaAs/AlGaAs heterostructures, fullerenes and other exotic materials.
- ab initio calculation of crystal properties, using powerful computers. Nowadays, first principle theories give access to a large number of properties of solids without relying on any empirical data: band structure, total energy, phonon spectrum, dielectric constant, effective charges, interatomic force constants... Our home-developed programmes and algorithms are currently applied to the study of $BaTi0_3$ and silicas as well as carbon-based materials like graphite, graphite intercalation compounds, fullerenes, nanotubes, and other novel forms of carbon.
- surface and interface properties of solids studied mainly with ionic spectrometries: ISS, SIMS and RBS. Elemental, functional and structural analyses of surfaces, interfaces and thin films by ionic spectrometries. A fundamental aspect concerns the study of the interaction of ions with solids. An applied aspect concerns the use of the ionic spectrometries to study phenomena occurring at solid surface and at interfaces between thin films and in composite materials (adhesion, diffusion, catalytic, electrical, rheological properties). Different materials and types of interfaces are currently

investigated: interaction thin film-substrate, modifications of polymer surfaces by different treatments (plasma, ion bombardment, flame), metallization of polymers, matrix-fiber interaction in thermoplastic composites, carbon black interaction with elastomers.

Scientific Output

Over the five last years the PCPM has published more than two hundred papers in international professional journals. It maintains close collaboration with many leading research groups in the U.S., Japan and Europe; joint research projects, joint papers, exchange of scientists. The PCPM is also a member of several CEE networks.

Cooperation with Industrial Firms

The collaboration with industry includes the development and characterization of new materials, as well as in the development of specific measurement techniques and theoretical tools. This cooperation includes joint research programmes.

Expertise and Equipment

Scientific and technical expertise in the following fields: electrical, thermal, magnetic and thermoelectric measurements of solids - Precise temperature measurement and control - Cryogenics and cryostat design (low and ultralow temperature) - Use of high magnetic fields - Very low noise AC and DC electrical measurements - Sample characterization - Clean room – micro and nanolithographies - Growth of nanoscale materials by electrodeposition – Vacuum and ultra high vacuum - Imaging TOF static SIMS, TOF ISS, combined ISS- SIMS in situ- connected to MBE facility - RBS facilities, LEED-AES, AFM, access to XPS, XRD, TEM, SEM, - Composites - Adhesion - High performance and parallel computing – Molecular modeeling.

APPENDIX II: Selection of Papers on Carbon Materials Published by the Team

Ab initio structure of Graphite Monofluoride $(CF)_n$
J.-C. Charlier, J.-P. Michenaud, and X. Gonze
Molecular Crystals and Liquid Crystals 245, 135-140 (1994)

First-principles study of the stacking effect on the electronic properties of graphite(s)
J.-C. Charlier, X. Gonze and J.-P. Michenaud
Carbon 32, 289-299 (1994)

Electronic band structure of multilayered carbon tubules
Ph. Lambin, L. Philippe, J.-C. Charlier and J.-P. Michenaud
Computational Materials Science 2, 350-356 (1994)

Electronic strucure of coaxial carbon tubules
Ph. Lambin, J.-C. Charlier and J.-P. Michenaud
Progress in Fullerene Research (Ed. H. Kuzmany, J. Fink, M. Mehring & S. Roth, World Scientific Publishing and Co. Pte. Ltd.,London), 130-134 (1994)

Graphite interplanar bonding : electronic delocalization and van der Waals interaction
J.-C. Charlier, X. Gonze and J.-P. Michenaud
Europhysics Letters 28, 403-408 (1994)

Temperature Dependence of the Conductivity in Conducting Polymer Composites.
X.B. Chen, J.P. Issi, M. Cassart, J. Devaux and D. Billaud
Polymer 35 (1994)5256

The stability of polypyrrole electrical conductivity
X. B. Chen, J. Devaux, J-P Issi and D. Billaud
Eur. Polym. J. 30 (1994) 809

Electrical resistance of carbon nanotube bundles
L. Langer, L. Stockman, J.P. Heremans, V. Bayot, C.H. Olk,
C. Van Haesendonck, Y. Bruynseraede and J.-P. Issi
J. Mater. Res. 9, 927-932 (1994)

Thermal conductivity of oriented polymer films
B. Nysten, P. Gonry, J-P Issi, L. Govaert and P. J. Lemstra
in Thermal Conductivity 22, edited by T. W. Tong, Technomic, (1994)

Anomalous transport properties of Graphite-$CoCl_2$
L. Piraux
Mol. Cryst. Liq. Cryst. 245, 67 (1994)

Electrical resistivity and magnetoresistance behavior below 50K of carbon-pich films of C-B-N alloys
L. Filipozzi, A. Marchand, A. Derré and L. Piraux
Ext. Abstr. of the International Conference on Carbon 94, p. 184

Structural and transport properties of fluorine-intercalated carbon fibers
A. Tressaud, V. Gupta, S. Flandrois, L. Piraux, L. Lozano, A. Marchand,
O. P. Bahl and R. B. Mathur
Ext. Abstr. of the International Conference on Carbon 94, p. 592

Fluorine intercalated carbon fibers : Structural and transport properties
A. Tressaud, V. Gupta, L. Piraux, L. Lozano, E. Marquestaut, S. Flandrois, A. Marchand and O. P. Bahl
Carbon 32, 1485 (1994)

Structural characterization of graphitization process in pyrocarbons

Rannou, V. Bayot and M. Lelaurain,
Carbon 32, (1994) 833-843.

First-principles study of carbon-nanotube solid-state packings
J.-C. Charlier, X. Gonze and J.-P. Michenaud
Europhysics Letters 29, 43-48 (1995)

Local order and electrical properties of boron carbonitride films
L. Filipozzi, A. Derré, J. Conard, L. Piraux and A. Marchand
Carbon 33, 1747 (1995)

Electrical resistivity of carbon nanotubes
L. Langer, V. Bayot, J.-P. Issi, L. Stockman, C. Van Haesendonck, Y. Bruynseraede,
J.P. Heremans and C.H. Olk
in *Physics and Chemistry of Fullerenes and Derivatives*, H. Kuzmany, J Fink, M. Mehring and S. Roth editors, World scientific (London, 1995) p565

Electrical measurements on submicronic synthetic conductors : carbon nanotubes
L. Langer, L. Stockman, J.P. Heremans, V. Bayot, C.H. Olk, C. Van Haesendonck,
Y. Bruynseraede, J.P. Issi
Synthetic Metals, 70 (1995) 1393

Electronic properties of carbon nanotubes : experimental results
J.-P. Issi, L. Langer, J. Heremans, C.H. Olk (Review paper)
Carbon, 33 (1995) 941

Physical Properties of fluorine and fluoride graphite intercalation compounds (Book chapter)
M. S. Dresselhaus, M. Endo and J-P. Issi
in *Chemistry, Physics and Appl. of Fluorine-Carbon and Fluoride-Carbon Compounds*,
Marcel Dekker, Inc. (New-York), T. Nakajima, editor (1995) 95

Intra- and interchain thermal conduction in polymers
B. Nysten, P. Gonry and J-P Issi
Synthetic Metals 69 (1995) 67

The conducting behavior and stability of conducting polymer composites
X. B. Chen, J. Devaux, J-P. Issi and D. Billaud
Polymer Engineering and Science 35 (1995) 637

Chemically oxidized polypyrrole: influence of the experimental conditions on its electrical conductivity and morphology
X. B. Chen, J. Devaux, J-P. Issi and D. Billaud
Polymer Engineering and Science 35 (1995) 642

Quantum transport in a multiwalled carbon nanotube
L. Langer, V. Bayot, E. Grivei, J.-P. Issi, J.P. Heremans, C.H. Olk, L. Stockman,
C. Van Haesendonck and Y. Bruynseraede
Phys. Rev. Letters 76, 479 (1996)

Structural and electronic properties of pentagon-heptagon pair defects in carbon nanotubes
J.-C. Charlier, T.W. Ebbesen and Ph. Lambin
Physical Review B 53, 11108-11113 (1996)

Electronic properties of carbon nanotubes with polygonized cross-sections
J.-C. Charlier, Ph. Lambin and T.W. Ebbesen
Physical Review B Rapid Communications 54, R8377-R8380 (1996)

Electrical conductivity of novel forms of carbon (Review paper)
J-C Charlier and J-P Issi
J. Physics and Chemistry of Solids, 57, 957 (1996)

Electrical and thermal conductivities of carbon fibers and their composites (Review paper)
J-P. Issi

in *Carbon and carbonaceous composite materials*, K. R. Palmer, D. T. Marx and
M.A. Wright, editors, World Scientific (London, 1996) pp 51-63

Microscopic growth mechanisms for carbon nanotubes
J.-C. Charlier, A. De Vita, X. Blase and R. Car
Science 275, 646-649 (1997)

Theoretical study of composite $B_xC_yN_z$ nanotube heterojunctions
X. Blase, J.-C. Charlier, A. De Vita and R. Car
Applied Physics Letters 70, 197-199 (1997)

Boron-doped nanotubes density of states from tunneling spectroscopy
D.L. Carroll, P. Kinlen, S. Raman, Ph. Redlich, M. Rühle, X. Blase,
J.-C. Charlier, S. Curran, S. Roth and P.M. Ajayan
Molecular Nanostructures (Ed. H. Kuzmany, J. Fink, M. Mehring & S. Roth, World Scientific Publishing and Co. Pte. Ltd., London), 477-481 (1997)

Electronic structure and localized states at carbon nanotube tips
D.L. Carroll, Ph. Redlich, P.M. Ajayan, J.-C. Charlier, X. Blase,
A. De Vita and R. Car
Physical Review Letters 78, 2811-2814 (1997)

Electronic properties of carbon nanotubes containing defects
Ph. Lambin, A.A. Lucas and J.-C. Charlier
Journal of Physics and Chemistry of Solids 58, 1833-1837 (1997)

The stability of polypyrrole and its composites
X. B. Chen, J. Devaux, J-P. Issi and D. Billaud
Journal of Materials Science 32(1997)1515

Nanowire bonding with the scanning tunneling microscope
C. Van Haesendonck, L. Stockman, R. J. M. Vullers, Y. Bruynseraede, L. Langer,
V. Bayot, E. Grivei, J.-P. Issi, J.P. Heremans and C.H. Olk
Surface Science 386, 279 (1997)

Synthesis of a $YBa_2Cu_3O_{7-x}$-Ag Composite using a Sol-Gel Method.
L.F. Admaiai, M. Ruwet, P. Grange, B. Delmon, M. Cassart and J.-P. Issi.
Journal of Materials Science 32, 2745 (1997)

Unusual behavior of the magnetoresistance properties of boron carbonitride films at low temperature L. Filipozzi, L. Piraux, A. Marchand, A. Derré, A. Adouard and M. Kinany-Alaoui J. Mater. Res. 12, 1711 (1997)

Electrical and thermal transport properties in carbon fibers (Book chapter)
J-P. Issi and B. Nysten

In *Carbon Fibers*, Marcel Dekker, Inc. (New-York), J-B. Donnet, S. Rebouillat,
T. K. Wang and J. C. M. Peng, editors (1998)

Frustration effects and microscopic growth mechanisms for BN nanotubes
X. Blase, A. De Vita, J.-C. Charlier and R. Car
Physical Review Letters 80, 1666-1669 (1998)

Electronic structure of carbon nanotubes with chiral symmetry
J.-C. Charlier and Ph. Lambin
Physical Review B Rapid Communications 57, R15037-R15039 (1998)

Morphologies and related electronic properties of carbon nanotubes
J.-C. Charlier
Journal of Materials Research 13, 2368-2379 (1998)

Surface reconstructions and dimensional changes in single-walled carbon nanotubes
P.M. Ajayan, V. Ravikumar and J.-C. Charlier
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Applied Physics A: Materials Science and Processing, 67, 79, (1998)

Study by a modified scanning electron microscope fractography of hydrogenation process in vapour grown carbon fibers
A. Madronero, M. Verdu, J-P. Issi, J. Martin-Benito Romero and C. Barba
Journal of Materials Science, 33, 2079 (1998)

Electrical transport properties in carbon nanotubes (Book Chapter)
J-P. Issi and J-C. Charlier

in *Science and technology of carbon nanotubes*, K. Tanaka, editor, Elsevier, London, (1998)

Surface treatments of vapor-grown carbon fibers produced on a substrate
Ph. Serp, J. L. Figueiredo, P. Bertrand and J-P. Issi
Carbon , 36, 1791 (1998)

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L. Duclaux, B. Ottaviani, L. Piraux, E. Grivei, J. P. Issi, F. Beguin and S. Flandrois
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Microscopic growth mechanisms for carbon and boron-nitride nanotubes
J.-C. Charlier, X. Blase, A. De Vita and R. Car
Applied Physics A 68, 267-273 (1999)

Structural and electronic properties of composite $B_xC_yN_z$ nanotubes and heterojunctions
X. Blase, J.-C. Charlier, A. De Vita and R. Car
Applied Physics A 68, 293-300 (1999)

Electronic structure at carbon nanotube tips
A. De Vita, J.-C. Charlier, X. Blase and R. Car
Applied Physics A 68, 283-286 (1999)

Surface treatments of vapor-grown carbon fibers produced on a substrate - Part II: Atomic force microscopy
J. L. Figueiredo, Ph. Serp, B. Nysten and J-P. Issi
Carbon, 37, 1809 (1999)

Tiny pipes with a big future
J.-C. Charlier
Science Spectra 17, 64-69 (1999)

Diamond formation by thermal activation of graphite
AV. Palnichenko, A. M. Jonas, J.-C. Charlier, A. S. Aronin and J.-P. Issi
Nature, 402, 162 (1999)

Carbon nanotubes: from macromolecules to nanotechnology
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P. Natl. Acad. Sci. USA, 96, 14199-14200 (1999)

Boron-mediated growth of long helicity-selected carbon nanotubes
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In « *Science and Application of Nanotubes* »
Fundamental Materials Research Series, Ed. Tomanek & Enbody,
Kluwer Academic/Plenum Publishers, NY, (2000), pp. 53-65.

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G. Dresselhaus, M.A. Pimenta, R. Saito, J.-C. Charlier,
S.D.M. Brown, P. Corio, A. Marucci and M.S. Dresselhaus
In « *Science and Application of Nanotubes* » Fundamental Materials Research Series, Ed. Tomanek & Enbody, Kluwer Academic/Plenum Publishers, NY, pp. 275-295, (2000)

The dynamic behavior of Nickel atoms in graphitic networks
F. Banhart, J.-C. Charlier and P.M. Ajayan
Physical Review Letters 84, 686-689 (2000)

New metallic allotropes of planar and tubular carbon
H. Terrones, M. Terrones, E. Hernandez, N. Grobert, J.-C. Charlier and P.M. Ajayan
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M. Terrones, H. Terrones, F. Banhart, J.-C. Charlier and P.M. Ajayan
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J-P. Issi
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J.-C.Charlier, mai 1994
"Transport électronique dans les nanotubes de carbone"
L.Langer, avril 1996
"Dynamique moléculaire et excitations atomiques dans la chaleur spécifique"
E.Grivei, février 1996