Nano-Architectured and Nanostructured Materials

Fabrication, Control and Properties

Edited by
Y. Champion and H.-J. Fecht
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Euromat is the biennial meeting of the Federation of European Materials Societies (FEMS) constituted by its 24 member societies in Europe. The 2003 meeting took place in Lausanne, Switzerland, and was organised by the French, the German and the Swiss member societies:

Société Française de Métallurgie et de Matériaux (SF2M)
Deutsche Gesellschaft für Materialkunde (DGM)
Schweizerischer Verband für Materialtechnik (SVMT)

The scientific programme of the EUROMAT 2003 congress was divided into 16 topics that in turn were substructured into 47 symposia. There will be no publication of a complete set of proceedings. The present volume of the Euromat Publication series refers to selected papers of the symposia

Fabrication, Control and Properties of Nano-Architectured Materials (E1)

and

Nanostructured Materials (E4)
Nano-Architectured and Nanostructured Materials

Fabrication, Control and Properties

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Preface

Nanotechnology is the creation and utilisation of materials, devices and systems through the control of matter on the nanometer-length scale. This is of great interest for science and engineering since fundamental physical properties change dramatically when the characteristic length scale of a particular property coincides with the structural length scale of the nanostructure of a material. This fundamental behaviour can generally be found for objects with different dimensionalities: 0-D (nanosized clusters), 1-D (nanowires), 2-D (thin-film-multilayers) and 3-D (bulk nanostructures) when the length scale of a microstructure is on the order of a few nanometers.

In all these cases, interfaces and surfaces which separate the different particles, layers and crystalline or non-crystalline domains from each other play the crucial role in controlling the properties and stability of nanostructures. Two effects are critical here:

- The atomic structure of the interface separating two domains and increasing the disorder in a nanostructure and
- Finite size effects of the domains themselves.

These two structural aspects are in general inherently coupled with each other. Thus, it is necessary to develop a fundamental understanding of the correlation between a property and the characteristic length scale of a nanostructure in order to improve a particular property and develop specific applications, such as for example, sensors, actuators, safety systems etc. Though extremely promising, the use of nano(structured) materials is still marginal because the fabrication of devices remains a challenge.

The table below summarises a few examples regarding the particular property of interest (in alphabetical order), the relevant physical phenomena and possible technological applications.

Size effects in interface controlled nano-architectured and nanostructured materials

<table>
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<th>Properties</th>
<th>Size dependent phenomena in a nanostructure</th>
<th>Applications</th>
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<td>Sensors, batteries</td>
</tr>
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<tr>
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</tr>
</tbody>
</table>

To attain these special properties, a complex architecture of the materials is generally necessary, obtained through unusual synthesis techniques and specific processing. Complexity stems from the nanometric size and the related surface and grain boundary energies, producing phenomena such as reaction, grain growth, interdiffusion, sintering, coalescence, agglomeration and that the process has to deal with.

This book contains 19 papers, selected from two symposia devoted to the science and engineering of nanomaterials and presented at the Euromat 2003 conference held in Lausanne (1-3 September).
The symposium « Nanostructured Materials » (organised by Hans-Jörg Fecht, Universität Ulm and Forschungszentrum Karlsruhe / Institute of Nanotechnology, Germany) was focused on materials and devices with a characteristic length scale (for example grain or cluster size, thickness of multilayer structures, quantum dots or wires) of less than 100 nanometers. The symposium aimed at reviewing the progress in the field of nanostructured materials and materials for nanotechnologies in terms of their synthesis and processing, as well as their structural, electronic, optical, mechanical, chemical and biological properties and, thus will further promote contact between basic research efforts and technological needs.

More specifically, objectives of the symposium « Fabrication, Control and Properties of Nano-Architected Materials » (organised by Yannick Champion, CNRS, Vitry-sur Seine, France) were to identify new nanometric architectures that would be of particular interest for applications and the technological route to reach them. Nano-architectures of interest are for optical, electrical, magnetic, mechanical properties and reactivity as well as for specific applications such as catalysis and medical diagnostic and drug delivery. Nano-architectures are metals, alloys, ceramics, semi-conductors, polymers or hybrids inorganic-polymers materials. The symposium placed special emphasis on crucial technical aspects of the fabrication, the control and the characterisation of complex nano-architectures. One session was devoted to the synthesis and properties of carbon nanotubes and Yannick Champion gratefully acknowledges Philippe Poulin, from the Centre de Recherche Paul Pascal (CNRS-Bordeaux) for organising this part of the symposium.

Fields and communities concerned by symposia were:
- Synthesis and processing for the fabrication of complex architectures
- Properties controlled by the architectures
- Characterisation and instruments
- Simulation and Modelling.

Related aspects were:
- Exploitation of the new properties of nanomaterials
- Versatility and ease of adaptation
- Nanostructure control for optimisation of properties
- Stability, manufacturing, ageing.

Articles in this book cover main topics discussed during the symposia and bring a good insight of our commitment which is to always produce more outstanding, well controlled and more realistic nano-architected and nanostructures materials.

The editors wish to thank the authors for their contributions and the publishers for their help in organising the book.

Yannick Champion, Hans-Jörg Fecht

September, 2004
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Multiwall Carbon Nanotubes Produced by Underwater Electric Arc

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1 Introduction

The submerged arc discharge in liquid media seems to be a cost effective and possibly upscalable method for growth of high quality multiwall carbon nanotubes (MWCNTs) and other nanomaterials. Using liquid nitrogen [1], water [2–8] or aqueous salt solution [2,5] instead of the traditional low pressure neutral gas atmosphere as reaction medium no sealed vacuum chamber is needed, the removal of the product and the replacement of the consumed electrodes is much easier.

In a previous paper [6] we reported an implementation of a continuous MWCNT production method based on underwater AC electric arc. The benefit of AC method compared to DC arc is that there is no deposition on the cathode, the product can be removed from the reaction container by the streaming water if suitable filtration is applied. Computer controlled stepper motors regulated the distance of the electrodes in order to maintain the arc, the voltage between the electrodes was used as feedback signal.

The problem of elimination of the impurities and side products occurs in case of most nanotube production methods. The suitable purification procedures usually depend on the method of nanotube production. High yield, low cost production methods of carbon nanotube raw material have only limited industrial significance if the selectivity can not be achieved or a cheap purification method is not available.

In this contribution we report some further observations on the properties of the underwater AC arc as nanotube synthesis method and the produced carbon nanostructures. Our efforts in purification of the raw material led to conclusions on the limitations of the conventional methods and the possible directions of further optimization of the process.

2 Experimental

An AC electric arc was generated between two identical electrodes submerged in deionised water in a glass vessel. In one case the electrodes were high purity graphite, in other case high purity carbon rods with 6 mm diameter. Two different geometries were compared, one is described in [6], in the other case the electrodes were in one line aligned horizontally. The temperature of the water in the vessel was monitored far from the arc. The arc was stable in the di-
scharge current range of 40–80 A with discharge voltage between 20–24 V. The stability was achieved after an initial period lasting 10–20 minutes depending on the supplied power if we started with room temperature water. Pre-heating the water up to 80 °C the period of initial instability was shortened down to a few minutes. It was possible to keep the apparatus running for 1–2 hours continuously. The current fluctuation was not more than 10%.

The product was filtered and dried at 100 °C for an hour. The weight of the dried product and the remained pieces of the electrodes was measured.

Three different chemical purification procedures were tried and we made some preliminary experiments for separation of the MWCNTs by sedimentation. Before these treatments, the product powder was carefully ground in agate mortar. The first method of purification was oxidation in flowing air at different temperatures. In the second case, 500 mg powder was dispersed in 100 ml of 1 M H2SO4. Then 1.75g KMnO4 was gradually added to the mixture. The solution was boiled for 5 hours then filtered. During the reaction MnO2 condensed, which was eliminated by dissolution in hydrochloric acid. Finally the sample was washed with distilled water, filtered and dried. Another way to purify the crude sample was the following: 150 mg powder was dispersed in mixed solution of 60 ml H2SO4 (98 %) and 40 ml of HNO3 (70 %). The solution was ultrasonicated then heated and kept at 150 °C and refluxed for 2 and 4 hours in two different experiments, respectively. Then the solution was filtered, the sample was washed with distilled water and dried. For the sedimentation experiments, 20 mg of crude product was added to 50 ml distilled water in a cylindrical glass flask. The flask was sonicated in an ultrasound bath with 70 W power for an hour then left to sediment for 1, 2 and 4 hours in three different experiments, respectively. The upper 2/3 of the suspension was carefully removed by pipette and examined separately.

Crude samples produced with different arc parameters, chemically purified samples and a control sample of the applied graphite electrode were analyzed with a differential thermogravimeter (Luxx NETZSCH STA 409 PC). The measurements were carried out at temperature rate of 2.5 °C/min from 20 °C to 1000 °C in 40 ml/min air and 20 ml/min He mixture flow.

The as prepared, purified and separated samples as well as the material of the graphite and carbon electrodes after grinding were characterized by Transmission Electron Microscopy (TEM) using a Philips CM 20 (Twin) microscope operating at 200 kV. For TEM investigations the powders were suspended in ethanol by ultrasonication and drop-dried on holey carbon film coated copper grids.

3 Results and Discussion

The TEM study showed no obvious difference in the composition of the material floating on the water surface, suspended in the water and the sediment product. The MWCNTs occur always agglomerated with carbon nano-onions, the so-called bucky onions. These agglomerations of MWCNTs and bucky onions (AMBs) ranging from a few hundred nanometers to several microns are bonded together chemically, presumably due to the presence of extra atomic oxygen and hydrogen in the arc plasma [7] as compared to the conventional arc growth technique. It is highly probable that the formation of agglomerated MWCNTs and nano-onions took place in the same time close to each other. The MWCNTs are well graphitized, closed at the ends with typical outer diameter of 10–35 nm and length of a few microns, however, the outer 1–2 walls are often damaged and they are partly covered with thin disordered material. This can also be
the consequence of the reactive formation ambient. Most of the bucky onions are nearly spherical with more or less polyhedral character; their typical dimensions are in the 20–50 nm range. Some nanoparticles are elongated, showing transitional shape towards MWCNTs. A TEM image of a part of a typical AMB is presented in Figure 1.

Figure 1: TEM image of an agglomeration of MWCNTs and bucky onions from a sample grown using 40 A arc current

In case of the graphite rods as starting material the samples consist also of graphite flakes with a wide range of dimensions: from a few ten nanometers to several ten microns. There are some clusters of amorphous carbon (soot) present in the samples but their amount is relatively small. While the proportion of MWCNTs and bucky onions in AMBs was found to be nearly constant (50–50 vol%) by TEM observations in all cases, the graphite flake content of the samples depends on the production conditions. Figure 2 shows a TEM image of an area where graphite flakes are dominant. Beyond the dependence on the arc current [6], we found that the instability of the arc leads to increased graphite flake amount. When the growth process was interrupted in the initial, unstable period, the rate of graphite was found as high as 80–90 % in the sample. This fact had raised the idea that graphite flakes were simply crumbled from the electrodes. Comparing the TEM images of the starting graphite electrode material to the underwater