SYNTHESIS OF CARBON-NANOTUBES AND THEIR APPLICATION IN "ANISOGRID LATTICE STRUCTURES"

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ABSTRACT

The unique carbon nanotubes properties (mechanical, electrical, thermal, etc.) are considered as a key factor for future improvement of technical characteristics of many engineering macro and nano systems.
A possible field of application of advanced composite materials is represented by innovative and recently introduced "Anisogrid Lattice Structures", realized in the form of a thin-walled shell (cylindrical or conical) with a system of a helical and circumferential ribs (with or without internal and external skin). Using this typology of structures, it is possible to satisfy high requirements of static resistance and stability (local and global buckling) in the minimum mass condition (Vasiliev Theory). Further improvements are expected by introducing nanotubes reinforced composites.
This new generation of structures and composite materials find concrete and interesting application in the aerospace technologies.
This paper reports the authors' studies on the synthesis (arc discharge and laser ablation methods), purification (oxidation and chemical etching) and morphological analysis (Optical, SEM, TEM, X-Ray and Chemical) of carbon nanotubes. Besides, the performance of anisogrid lattice shells reinforced with nanotubes composites, simulated by both analytical and FEM analysis, are discussed.

1. INTRODUCTION

The utilization of carbon nanotubes (CN) improves the expected characteristics and performances of many advanced engineering systems (mechanical, biomedical, nanosensors, defense, etc.). The primary technical goal under study is the production of high quantity of carbon nanotubes jointly with high degree of purification and alignment. For each specific application the morphology of the CN results a key factor. For example, in electronic devices (MEMS/NEMS) low quantity of CN are requested (but with high alignment degree), on the contrary, for structural application the availability of high quantity results important, but the alignment is not a principal requirement. The costs of production is a remarkable problem, which hampers the replacement of traditional materials with composite CN reinforced. Moreover, the study of the different synthesis techniques results necessary, aiming to obtain characteristics and morphology fitting with the final requirements of the devices to be realized. The experimental activities is aimed to determine the process parameters and the test configuration able to optimize the results. In this contest, the morphological analysis (SEM, TEM, EDX, Optical) is the primary instrument for the CN characterization.
The typical synthesis process presently more known and developed are:

1. Arc discharge in the controlled atmosphere (using inert gases: argon, helium)
2. Arc discharge water immersed (the insert gas is not required)
3. Laser ablation (CO_2 & Nd-Yag)
4. CVD (Chemical Vapor Deposition).

For structural applications, the synthesis by arc discharge and laser ablation result the most suitable methodologies, as high quantity production of CN is possible. The CN's production with CVD is lower but, theoretically, the alignment is better, therefore this last methodology is preferentially finalized to nanoelectronics devices.
The Authors studied and developed the facilities (fig. 1) relative the techniques 1-3, as the CVD is not suitable for structural application, reported in this paper.

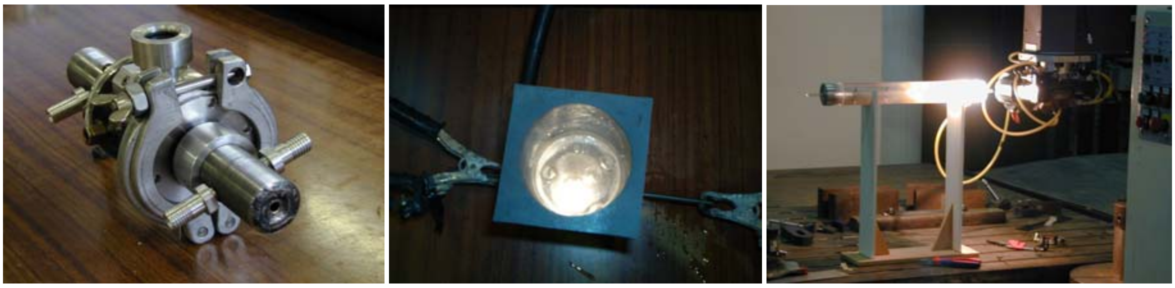

Fig. 1. The arc discharge and laser ablation facilities developed

A set of experimental test is performed to evaluate, by electronics microscopy, the different nanomaterials synthesized.
Typical parameters used in the arc discharge in controlled atmosphere, are:

- Dc voltage (20-25 V)
- Amperage: 50-60 A
- Inert environment (helium gas, flow pressure: 0.2 bar).

Parameters used for the arc discharge in water immersion are:

- Dc voltage (20-25 V)
- Amperage: 60-90 A
- De-ionized water.

Parameters for the laser ablation (CO_2) are:

- Power: 900 W
- Wave length 10.6 µm
- Argon flow: 60 l/min

In particular, the following parameters are closely controlled:

- The electrodes gap
- The arc stability
- The synthesis time
- The environment (gas pressure, gas analysis, temperature).

The type of graphite used in the process influences the synthesis results. In fact, pure graphite (> 99.9%) or drugged with a catalysts (cobalt, yttrium, nickel) can be chosen. The purpose is to improve the CN production. Moreover, different chemical compositions can be used to control the morphologies (i.e. single-wall CN or multi-wall CN). The various electrodes configurations used in arc discharge (fig. 2) allow to obtain different physical behaviours during the process (arc stability, uniform distribution of the temperature in the region of the synthesis, major control of the parameters employed).

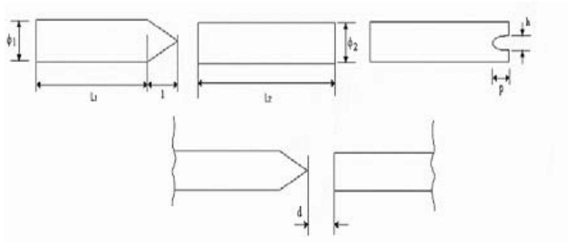

Fig. 2. Different electrodes configuration

2. EXPERIMENTAL RESULTS

Whit reference to the problems involved in the morphological analysis of the synthesized materials, special procedures for samples preparation are developed. The goal is to acquire the capabilities to identifie, simply using the optical microscopy, the target graphite zone where the presence of carbon nanotubes is higher. By using standard procedures, numerous samples must be analyzed, using SEM and TEM, in order to understand the macroscopic characteristic of the deposit containing CN. For example in the fig. 3 an optical imagine is reported, where it is possible to identify a black zone characterized by a major presence of CN, as confirmed by SEM studies. The surface of the black zone is approximately 16 mm^2. Besides, the same figure illustrates the different electrodes configurations used in the arc discharge tests.

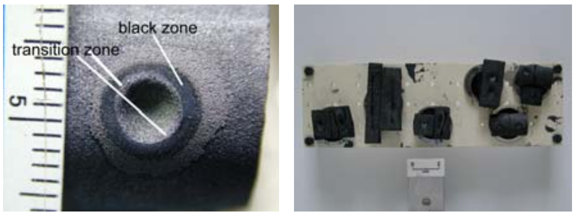

Fig. 3. The electrode used in the arc discharge facility and the different electrodes configuration used

Fig. 4 shows the CN produced by arc discharge in controlled atmosphere, and fig. 5 CN produced by arc discharge immersed in water and laser ablation. The high quantity and the high purification degree of the nanomaterials produced can be observed. No purification step was used. On the contrary, the alignment degree is not excellent, but for structural applications this parameter is not highly significant, as discussed.

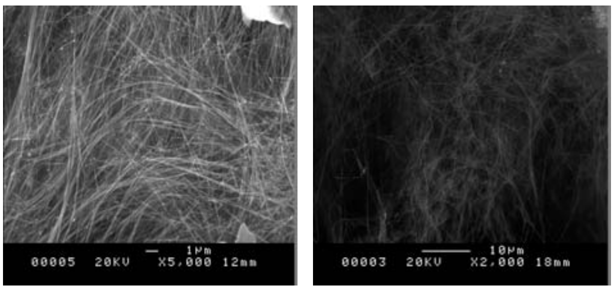

Fig. 4. CN produced

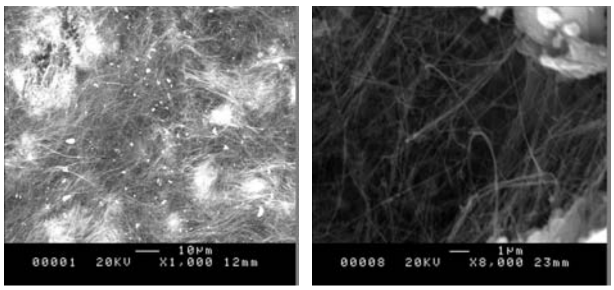

Fig. 5. CN produced

Finally, fig. 6 shows the transition between the zone where the synthesis happened (see fig. 3) and the central electrode region in which the local experimental conditions are not favourable for the production of nanotubes. TEM observations are performed (fig. 7) to evaluate the effective presence of CN. The chemical composition of the nanomaterials is determined by EDX analysis (fig.7).

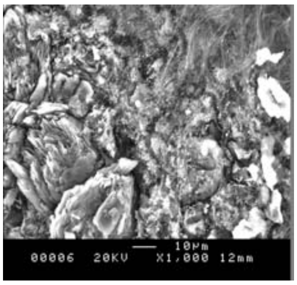

Fig. 6. Transition zone in the electrode surface showed in fig. 3

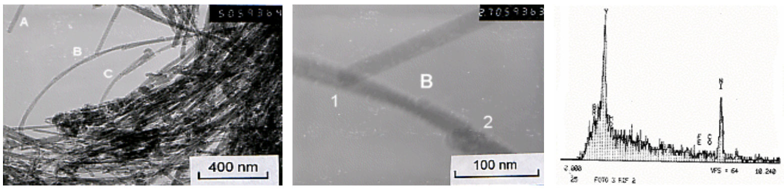

Fig. 7. TEM and EDX analysis (ref. figures 4÷6)

A purification step of CN's after their synthesis is necessary to eliminate all impurities (non-transformed residual graphite, catalysts, fullerene, etc.). The oxidation is a typical purification techniques adopted. A DTA-TG purification tests are performed with the following parameters:

- 50 mg of synthesized material
- oxidizing flow: N_2 90%, O_2 10 %
- T_{max}: 780 °C
- Time: 5 h.

Fig. 8 and fig. 9 show, respectively: the facilities employed and the DTA-TG curve test obtained, the SEM morphologies of the CN before and after the purification.

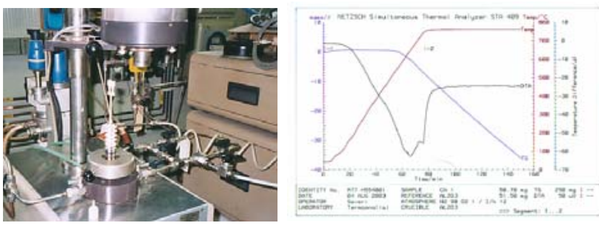

Fig. 8. DTA-TG facility and test curve results

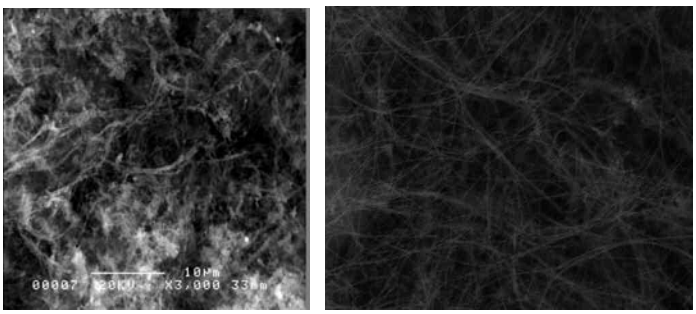

Fig. 9. SEM analysis of the CN before and after the purification (DTA-TG)

By using ultrasound, as a purification methodology, the CN show the tendency to be cut, due to the vibrations and the thermal stresses developed. The fig. 10 illustrates this phenomena. This technique could be very interesting as purification methodology, as results simple, cheaper and fast, but requires a critical control in the test parameters adopted.

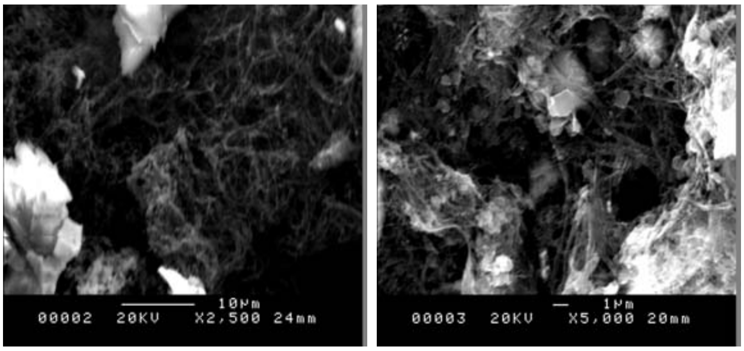

Fig. 10. SEM analysis of the CN before and after the purification with ultrasound

3. COMPOSITE MATERIALS CARBON NANOTUBES REINFORCED

In the aerospace application, the materials used must to be resistant and light. The composites are able to satisfy the above requirements. Besides, thank to the mechanical CN's properties (theoretical Young Modulus: 1 TPa) new advanced composite materials can be designed. Others properties of the CN are also important. The problems relative to the practical realization of composite nanomaterials, CN reinforced, are:

- selection of the materials used (resin, curing agent, nanometric particles)
- methodologies adopted for the samples preparation for SEM/TEM analysis
- determination of optimal curing conditions
- uniform distribution of the nanometric particles and carbon nanotubes embedded in the polymeric matrix
- qualification by mechanical test (dynamic and static)
- morphological analysis
- study of the mechanical fracture behaviour of the composite
- improvement of the characteristics of the composite
- numerical analysis of the composite behaviour
- application of advanced composites (carbon nanotubes reinforced) in the aerospace structures

Fig. 11 shows the samples produced for mechanical testing and facilities for tensile tests. The experimental results obtained by dynamic analysis (resilience test) and tensile test demonstrate that the Young's Modulus improvement is ≥ 12%, when passing from resin sample non reinforced and the sample reinforced by addition of nanometric carbon particles (CN and others). The optical analysis of the fracture surface is reported in fig. 11.

Fig. 11. Samples produced, traction test facility, optical analysis of the fracture section

Figure 12 illustrates the SEM studies on the mechanical behaviour of samples containing different quantity of nano carbon particles dispersed in the epoxy matrix. In particular has been observed that increasing the above nano particles quantity (> 20 in wt) the preferential line fracture propagation are developed in the sample. Instead, fig. 13 shows the morphological aspect of the fracture section. The radial line shown is due to a local uncompleted curing caused by pour homogeneity in the chemical composition (different reticulation degree between epoxy resin – curing agent – nano carbon particles).

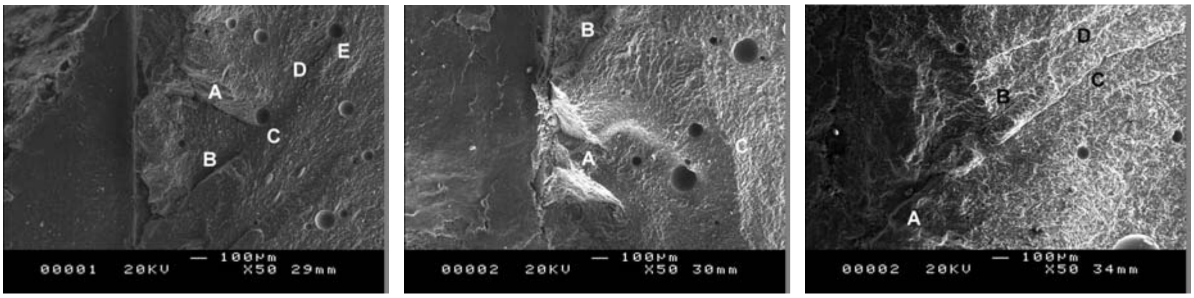

Fig. 12. SEM analysis of the fracture section


Fig. 13. optical analysis of the fracture section and the nano structured thin films

The realization of thin films nano structured is requested for electronic applications (MEMS/NEMS). In fig. 13 two thin films, CN reinforced, are reported.
The Authors are presently working on the development of composite samples containing only carbon nanotubes dispersed in the epoxy matrix.

4. ANISOGRID LATTICE STRUCTURES

The Anisogrid lattice structures (fig. 14) are new advanced aerospace elements characterized by helicoidal ribs, resistant to the applied load, and circumferential ribs, which ensure stability against local and/or global buckling satisfying the minimum mass condition (as per Vasiliev Theory). The above requirements must be verified by numerical and FEM analysis (Finite Elements Model) (fig. 14). The loads and constraints configurations that satisfy the Vasiliev model were determined.

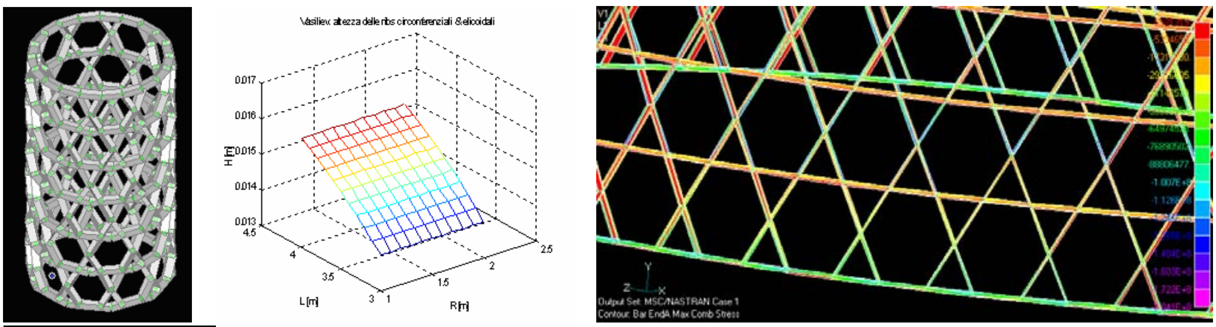

Fig. 14. The anisogrid and the examples of numerical and FEM analysis useful to validate the Vasiliev model

It’s useful to evaluate the variation of ribs dimension (as per Vasiliev model) using different materials: **a)** aluminium alloy Al 2024, **b)** composite epoxy resin carbon fibres reinforced (Hs/Ep), **c)** composite epoxy resin reinforced by carbon fibres and by a dispersion of carbon nanotubes, 5% by weight.
A numerical example is applied on a cylindrical anisogrid lattice structure (radius **R** = 1.5 m, height **H** = 4 m, applied load **P** = 3 MN, tab. 1).

Tab. 1. Structure Mass calculated for different materials

MATERIAL	Al 2024	Hs/Ep	Hs/Ep + 5% CN
YOUNG’S MODULUS [Pa]	70E9	12E10	16E10
MASS [Kg]	206.3	84.1	69.7

The data reported in tab. 1 show that the use of carbon nanotubes allows a significant mass reduction, considering equal mechanical behaviour of the lattice anisogrid structure. Combining a design based on the Vasiliev model with the mechanical characteristic offered by carbon nanotubes, it is possible to realise an aerospace structural element characterized by very interesting performance. This new advanced materials and structures find several application in various engineering sectors. Finally, flat and cylindrical anisogrid prototypes (fig. 15 & 16) are developed with the following techniques:

- CAD design of the elements,
- rapid prototyping of the positive elements,
- realization of the negative silicon mould,
- manufacturing (hand lay-up and filament winding) of the structures.

Fig. 15. Flat anisogrid element manufacturing procedure

Fig. 16. Cylindrical anisogrid element manufacturing procedure

CONCLUSION

High productivity of carbon nanotubes characterised by very good purification degree can be obtained, by optimization of controlling process parameters. The arc discharge and laser ablation facilities were developed. The purification test performed (oxidation and ultrasound etching after the synthesis operation) shows that purification is a critical step. The carbon nanotubes finally obtained must be pure enough to be successfully integrated in the advanced nanotech systems (composite, nanodevices, electronics facilities, sensors, biomedical applications, etc.). Suitable morphological analysis techniques (with electronics microscopy) were developed as an important instrument in the CN characterization.

The utilisation of Vasiliev theory allows to design innovate structures, anisogrid lattice, satisfying the requirements of minimum mass in the global and local stability conditions. The load and constraint configuration that satisfy the stability and static resistance conditions are determined by FEM analysis.
The addition of carbon nanotubes in a composite material (epoxy fibre reinforced polymers) improves the mechanical properties. In particular, the increase of the Young Modulus offers the possibility to further reduce the mass of the structure.
As final results, the combination of both the innovative design of anisogrid lattice structures and the utilisation of composite materials containing carbon nanotubes, allows to obtain a strong overall mass reduction of the structural component, maintaining the stability requirements.

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