Study of Ni clusters electrodeposited on Carbon fibres by Transmission Electron Microscopy

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Summary
In this work a TEM characterization is reported in order to investigate about the morphology and the structure of electrodeposited Ni on a carbon substrate. In particular more attention has been paid on the nature of the interface between electrodeposited Ni clusters and a PAN carbon-based fibre in order to understand and to explain better the strong adhesion of this electrodeposit to the substrate. FIB preparation for TEM observation was required to obtain this kind of information about the interface of this materials system with this particular geometry.
From our results, with the support of findings obtained with other characterization techniques, the strong bond of the electrodeposit to the substrate can be related to the presence of Ni hydroxides at the interface. So it can be confirmed that electrodeposited Ni, thank to its good adhesion to the substrate due to the hydroxides presence, is a suitable catalyst in the catalysed growth of carbon nanostructures.

Keywords: Ni clusters, electrodeposition, TEM, catalysts, catalysed carbon nanostructures.

Introduction

In the study of the growth of carbon nanostructures and in particular of carbon nanotubes, the catalysts have a key role. In fact it has been demonstrated that the shape of carbon nanotubes and nanofilaments depends on the catalysts composition as well as on deposition parameters (Martin-Gullon *et al.*, 2006; Kaatz *et al.*, 2006; de Lucas *et al.*, 2006). Moreover, the performances of the catalytic particles are dramatically influenced by both physical and chemical interactions with the substrate. When there is a physical interaction between the support and the catalytic material and the adhesion of the catalytic particles to the substrate is very good, it is expected that catalysts coalescence phenomena during the growth process of carbon nanotubes, generally carried out at relatively high temperature, can be avoided. For this reason it is proved essential to deeply study the catalyst–substrate interface and its microstructure, in order to understand the catalytic particles role and to optimize the whole carbon nanostructures growth process.

In this work our attention is focused on the interface between a carbon substrate, such as carbon fibres (exactly PAN fibres), and catalytic Ni clusters synthesized by electrodeposition. This technique is very versatile, rapid and inexpensive and can allow, only by controlling specifically the process parameters, the deposition of both a continuous film or of particles also on complex and convoluted supports. As far as the adherence of the electrodeposited clusters on a substrate, the plating conditions, the substrate treatment and the electrolytic bath composition can be optimized in order to obtain a well adherent metallic coating (Reddy *et al.*, 1998; Bockris, 1998).

The high catalytic activity of Ni and the properties of Carbon make these materials a very inter-

esting system; in particular these Ni particles electrodeposited on carbon substrates were successfully used in catalysed carbon nanotubes growth, as reported in other papers (De Riccardis *et al.*, 2005; Dikonimos Makris *et al.*, 2005). Moreover this electrodeposited material has shown a very good adhesion on carbon paper substrate and on PAN carbon-based fibres (Dikominos Makris *et al.*, 2005; De Riccardis and Carbone, 2006).

In order to understand better the mechanism of this strong adhesion, since Carbon and Nickel form no stable carbides (Massalski, 1990), in this work we investigated in detail about the interface between electrodeposited Ni and substrate by means of Transmission Electron Microscopy (TEM). This technique reveals invaluable in the structural and analytical characterization for its high spatial resolution and so it is successful and widely used also for the study of the interface between different materials constituents.

Materials and Methods

Ni electrodeposition on a bundle of PAN carbon-based fibres (in general obtained by pyrolysis of Polyacrylonitrile) was performed by using a cylindrical electrolytic cell with a cylindrical assembly of PAN fibres as working electrode and a coaxial Pt spiral as counter-electrode, in order to get a uniform deposition along all the fibre length and diameter. Before the use, PAN fibres were cut from a woven fabric and were cleaned from binder with a thermal treatment at 650°C for 1 hr in air, then washed with acetone and ethyl alcohol and finally rinsed with deionised water. A solution of 0.5 M $NiCl_2 \bullet 6H_2O$ with deionised water was prepared and HCl was added to adjust pH to 3.0. Other experimental details and parameters about Ni electrodeposition on PAN carbon-based fibres can be found elsewhere (De Riccardis *et al.*, 2009).

TEM analysis was performed by the transmission electron microscope TECNAI G^2 F30, operating at 300 kV and with a point resolution of 0.205 nm, equipped with a Schottky Field Emission source and with a STEM attachment with Bright Field, Dark Field and High Angle Annular Dark Field Detectors. The analytical capabilities consist in a solid state X-Ray detector (EDAX) with an ultra-thin window for EDS chemical analyses and a Gatan Imaging Filter (GIF) to obtain electron energy loss spectra and energy filtered images.

Since the more wide interest was directed to the interface between electrodeposited Ni clusters and PAN carbon-based fibres, because of the specific geometry of the substrate, a longitudinal cross-section was prepared with the FEI Strata 400 FIB/SEM system with the *in situ* Lift Out technique. A bundle of fibres was fixed on a stub by means of carbon glue to choose only a suitable fibre. First of all, two different thin Pt layers were deposited, the first one by the Electron beam and the second one by the Ion beam, in order to protect the electrodeposited Ni from possible damage during TEM lamella preparation. Then the lamella was cut across the longitudinal section of the carbon fibre. Subsequently it was milled on the back side and on the front side at an acceleration voltage of 30 kV and with an ion beam current of 9 nA and then with currents of 2.8 nA and 0.92 nA. At about 1.5 µm of thickness, the lamella was lifted off from the bulk of the fibre and transferred, by means of a micromanipulator needle (Omniprobe), to a TEM sample holder for the final thinning to a thickness of less than 100 nm and for final cleaning at low acceleration voltage and beam current, in order to reduce to few nanometers the amorphous layer on both sides of the lamella. In Figure 1 is reported an overview of the longitudinal section of the sample obtained with FIB, while in the inset there is an image of the step of separation of the lamella from the fibre.

Conventional TEM images (Bright Field Images) were obtained from many areas of the sample in order to analyse the global morphology of the electrodeposited Ni clusters, such as size, shape and uniformity of size, while High Resolution TEM images gave useful information about their microstructure and the nature of the interface.

Besides some High Angle Annular Dark Field (HAADF) STEM images were also taken from the specimen; in general this kind of images can highlight chemical differences among many characteristic details of the observed sample because of their contrast sensible to the local chemical composition and local thickness of the observed region. In this way also Energy Dispersive Spectrometry (EDS) was carried out for chemical analysis with the electron beam focused both

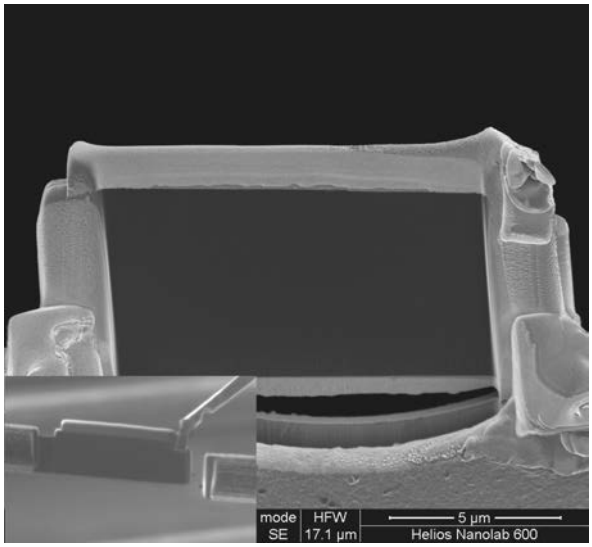

Figure 1. An overview of the longitudinal cross-section obtained at the end of FIB preparation, while in the inset there is a step of separation of the lamella from the fibre.

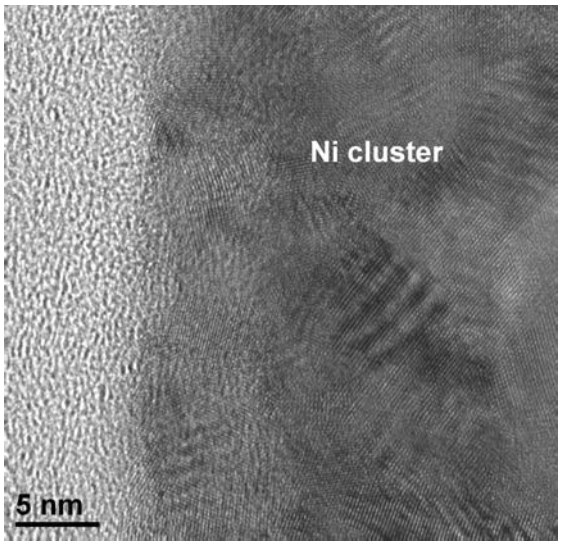

Figure 3. A typical HRTEM image of the interface between a Ni cluster and the carbon substrate. Lattice fringes and Moirè fringes can be noted in the cluster because of its polycristalline structure.

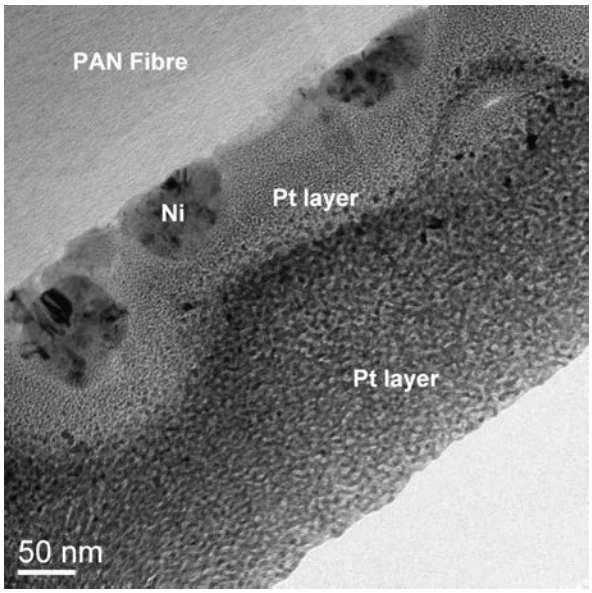

Figure 2. A BF TEM image of a small area of the longitudinal cross section of the sample: the two layers of Pt, due to the FIB preparation, several Ni clusters and the PAN carbon-based fibre are indicated.

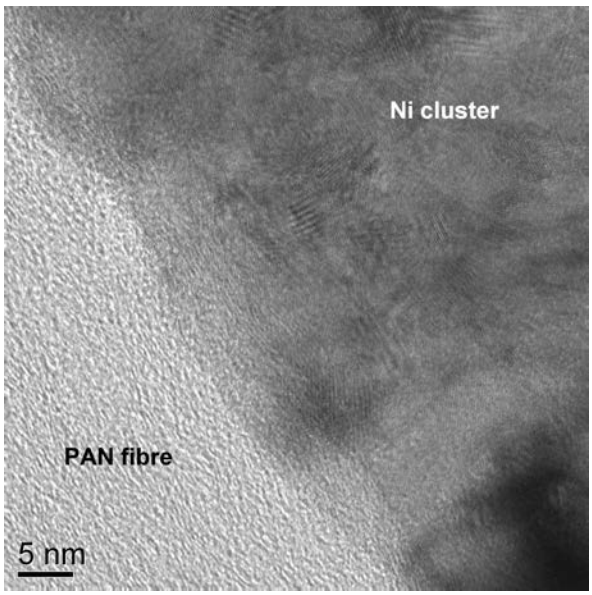

Figure 4. A HRTEM image of an area of the interface between another Ni cluster and the PAN fibre.

on many Ni clusters and on their interfaces with the substrate in order to detect any chemical difference.

Results

Conventional Bright Field (BF) images show that the electrodeposited Ni consists of several clusters. Their shape results globular and differently sized, with a width in the range of 60-90 nm at the base and a height between 50 and 80 nm, as shown in a typical BF image of an area of the longitudinal section of a PAN fibre (Figure 2). In this same image the two thin layers of Pt, different in appearance due to the source used for their deposition, are also well visible.

The electrodeposited Ni clusters are polycrystalline with a grain size of few nanometers. Figure 3 is a typical HRTEM image of a small area of the interface between a Ni cluster and the PAN fibre

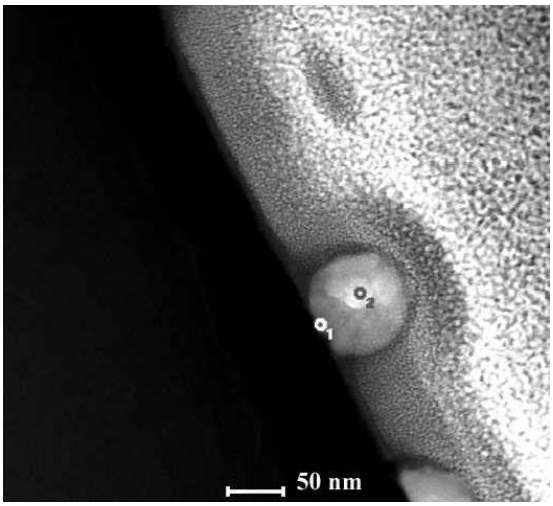

Figure 5. A HAADF image of a region of the longitudinal cross-section where the different materials can be detected for their compositional contrast. There are also the local points from which the EDS spectra were collected.

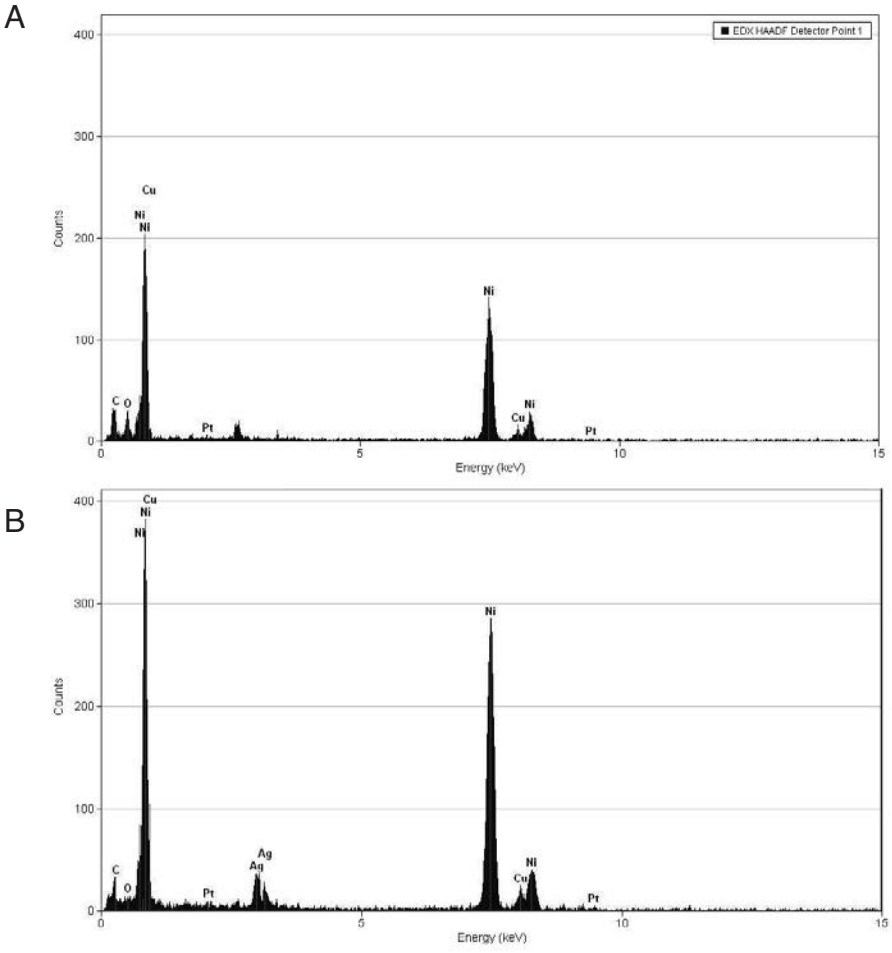

Figure 6. Two EDS spectra collected with the beam focused on a point at the interface (a) and on a point in the Ni cluster (b).

substrate. In this image there is a clear evidence of the polycrystalline nature of the cluster; in fact, in the same cluster some regions, well oriented with respect to the electron beam, are characterized by the presence of reticular fringes, while other areas show the Moirè fringes due the overlapping of more grains.

Besides, by considering the Fourier Transform of some crystalline areas in the cluster, a typical ring electron diffraction pattern can be obtained where the ratio of the diameters of the rings can be related to the f.c.c. structure of Ni.

In order to study more in details the structure of the interface between the carbon substrate and the clusters, some HRTEM micrographs were taken along all the interface in correspondence of several clusters. Typical example of these HRTEM images is in Figure 4 where the structure of the interface is not particularly evident, despite the favourable observation geometry. The HRTEM images of the same regions did not shown any differences also after having tilted the samples, expedient made in order to exclude an detrimental influence on the appearance of the interface due to a not well perpendicular interface with respect to the electron beam.

For further chemical analysis of the interface, some EDS spectra were collected with the electron beam focused in spot on points in the interior of several clusters and on points of their interface with the carbon fibre. In Figure 5 it is shown a HAADF STEM image of electrodeposited Ni on a PAN fibre, while in Figures 6a and 6b the EDS spectra collected from the interface and the cluster, respectively, are reported. In all EDS spectra, besides the characteristic X rays peaks of Cu (due to the grid) and those of Pt and Ag (due to the FIB preparation), characteristic X rays peaks of Ni, O and C are always present. By comparing the ratio between the integrated intensity of the Ok and Nik peaks (after background subtraction), acquired from the clusters and at their interface, a higher O content at this interface results systematically.

Discussion and Conclusion

FIB preparation results essential for TEM observation of this material system with an unusual geometry. TEM characterization was successfully carried out especially as far as the study of the interface between the electrodeposited Ni and the PAN carbon-based fibre, which was the most interesting requested information. Conventional TEM images and HRTEM images revealed the formation of many lenticular polycrystalline clusters. About the structure of the interface, no evident and clear interface could be seen, but more interesting was the analytical finding obtained from local EDS spectra acquisition, that is a higher content of Oxygen at the interface. This finding is in agreement with the results of the other more specific analytical studies reported elsewhere (De Riccardis *et al.*, 2008, 2009) and adds a piece of information for the interpretation of the strong adhesion of electrodeposited Ni catalyst to the substrate. In fact the bond between Ni clusters and Carbon substrate is based on Ni hydroxides, which can justify this very good adherence. The result about this catalytic electrodeposited Ni is interesting because it is suitable for the understanding of the influence of catalysts in catalysed growth process of carbon nanostructures.

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