TEM Characterization of Carbon Nanoshells Obtained from Leaching Carbonyl Nickel Metal Powders

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Abstract. Certain carbonyl nickel powders manufactured by the Mond chemical vapour deposition (CVD) process are coated with a nanometric layer of graphitic carbon. Through a simple chemical process of acid leaching of the nickel metal a dry filtrate is obtained, which consists of carbon nanopowder. As imaged in a transmission electron microscope (TEM), the powder consists of hollow carbon shells, termed carbon nanoshells (CNS) that are replicas of the nickel particulates. The shell thickness may vary from a few nanometers to tens of nanometers. Each carbon shell is composed of layered nanocrystals of turbostratic graphite distinguished by the presence of a high density of defects, such that the basal planes tend to follow the curvature of the original Ni core. EELS analysis showed that the electronic character of the CNS is closer to that of graphite than to amorphous carbon.

1. Introduction

Commercial nickel metal powders, which are commonly obtained by chemical vapour deposition (CVD) of nickel metal from nickel tetracarbonyl, are composed of high-purity nickel and can be used to enhance conductivity in the electrodes of rechargeable batteries. In an earlier study to characterize Ni powders [1], it was found that certain batches were coated with a surface layer of carbon, which comes from the organic carbonyl precursor. Although the carbon content is typically low, ~0.3 wt %, experimental batches have been produced for which the carbon content is increased to nearly 2 wt %. By leaching out the Ni with nitric acid it has since proved possible to prepare samples of carbon nanoshells (CNS), which have been characterized using TEM.

2. Experimental

Two carbonyl Ni powders, manufactured by INCO at their Speciality Metals Division and having different C concentrations, were used for the preparation of the leached carbon nanoshells. One powder, Ni210, was from a commercial Inco Type 210 batch containing 0.28 w % C, whilst the other was an experimental powder, Ni210X, contained 1.8 w % C. The carbon nanoshells were produced by leaching the Ni from the nickel powder, using reagent-grade nitric acid, yielding powder labelled C210 and C210X, respectively.

Powder specimens were examined in a Philips CM20FEG transmission electron microscope (TEM), equipped with (a) a Gatan Imaging Filter (GIF) model 678, that also permits electron energy-loss spectroscopy (EELS), and (b) an Oxford Instruments Link thin-window energy dispersive X-ray (EDX) detector with an Inca analyzing system. The carbon nanophase powder was thin enough that
the TEM characterization could be carried out using as-received powder that was dispersed on a holey carbon film.

3. Results
Figure 1 shows a low magnification, secondary electron (SE) scanned image of C210X CNS powder and a high-resolution (HREM) image from the as-leached batch C210. The SE image (as well as stereoscopic TEM micrographs) illustrated the similarity of the 3-dimensional morphology of the nanoshells to that of the pre-existing Ni powder. Smaller fragments of nanoshells were also observed. A selected area diffraction (SAD) pattern that was recorded from sample C210X could be indexed according to hexagonal graphite. The high-resolution images showed that the basal planes in the curved shells were oriented approximately parallel to the original underlying Ni. A high density of lattice defects could be inferred from all high-resolution images, including dislocations with components of Burgers vector $b$ along the $c$-axis. The wall thickness of the C210 material was typically $3 \sim 50$ nm; that in the C210X nanoshells was $10 \sim 70$ nm.

![Figure 1. Electron micrographs of carbon nanoshells powder; (a) low magnification SE scanning image, type C210X, (b) HREM image showing the basal planes of graphite in type C210 material.](image)

EDX microanalysis in the TEM (figure 2) revealed the presence of low levels of Ni, Si and O. The Ni presumably originates from Ni atoms that remain bound to the surfaces of the graphite after the leaching process because metallic Ni was not observed as a separate phase in the TEM. The presence of O was confirmed using EELS, which sometimes also revealed a very weak contribution from nitrogen (figure 3). The Si and Cu probably arise from a hole-count effect from the carbon support film and the Cu grid, respectively.

![Figure 2. EDX spectrum from sample C210X.](image)
Figure 3. EELS spectrum from type C210 CNS, showing the presence of O plus a low level of N.

Plasmon peaks in low-loss EEL spectra are shown in figure 4 for the C210X nanoshells, together with high-purity (H-P) graphite and amorphous carbon (from the C support film). Averages of spectra from the CNS powder gave peak energies of 6.15 eV and 26.05 eV, compared to 6.55 eV and 27.2 eV for the H-P graphite and 23.15 eV for amorphous C. The lower energy peaks correspond to the $\pi$ resonance peak (absent from the amorphous carbon), whilst the higher energy peaks correspond to the $(\pi + \sigma)$ plasmon. The results indicate that the electronic structure of the CNS is much closer to that for graphite than for amorphous C. Similar results were obtained from examining the appearance of the CK edges.

Figure 4. A comparison of low-loss plasmon spectra from C210X CNS with those from graphite and amorphous C.
4. Discussion
The leaching of nickel powder involves a fairly violent reaction, so that the resulting nanoshells are a mixture of regions that had remained more or less intact during the Ni dissolution process, plus smaller fragments caused by mechanical break up. It seems most likely that the acid gains ingress to attack the Ni through regions of the graphite coating that are thinnest or discontinuous. This picture is supported by the frequent observation of open holes at the end of the nanoshell filaments. In particular, the fact that the walls of these regions taper down virtually to a sharp edge indicates that after initial ingress of the acid leach, violent gas evolution produces high internal pressure that causes the fracture of the carbon nanoshells at regions of weakness such as the necks between some of the original Ni crystals.

It is clear that the graphite that forms on the surfaces of the Ni powders always deposits such that the (0001) basal planes follow the curvature of the underlying Ni. In order for this to happen, the planes must contain edge dislocations that allow tilting of the planes to occur, as shown in the HREM images. The stresses are such that they can be relieved by the generation of tilt sub-boundaries composed of dislocations with a component of $b$ along the $a$-axes.

It is apparent from the HREM images of the basal planes that many dislocations having a component of $b$ along the $c$-axis are also present. The nucleation of dislocations having a large Burgers vector corresponding to one whole basal plane (known as $c$-type dislocations) may be unlikely because the energy of a dislocation follows a squared relationship with respect to $b$. The easier nucleation of lower energy ($c + a$) dislocations may therefore be favored. Dislocations of this type could be aligned in walls to form tilt boundaries as deposition of the graphitic planes progresses and, because of the component of $b$ along an $a$-axis, would compensate for the stresses created by the curvature of the original Ni substrate.

An intriguing feature of the graphite that is formed on the underlying Ni is that it bears no epitaxial relationship to the underlying Ni surfaces. The reasons for this most likely arise from the highly anisotropic crystal structure of graphite and the fact that graphite is the equilibrium phase under the conditions of deposition. When carbon atoms are deposited onto the Ni surface, there is an overwhelming tendency for them to form planar (0001) clusters as a result of the strongly overlapping $sp^2$ hybridized $\pi$ orbitals. There is little tendency for the C atoms to bond with the substrate, because Ni is not a strong carbide former.

5. Summary
Acid leaching of carbon-coated Ni metal powder can be used to create carbon nanoshells. Detailed examination by TEM shows that the powder consists of hollow graphitic shells that are replicas of the Ni powder, such that the basal planes follow the curvature of the underlying Ni. EELS spectra show that the electronic structure of the carbon is similar to that of graphite and electron diffraction data indicate that it is best described as turbostratic graphite.

References
[1] Carpenter GJC, Wronski ZS 2004 J. Nanoparticle Research 6, 215-221.