ETEM Issues and Opportunities for Dynamic *In-situ* Experiments

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Many dynamic processes do not occur in nature, science or industry in a typical TEM high (and sometimes not so high) vacuum environment. Dynamic *in-situ* data related to the real world need to be obtained under CONTROLLED conditions of gas/vapor/liquid environment and temperature. In the ETEM* (Environmental Transmission Electron Microscope), the specimen – but nothing much else – is shared between the chemical reactor on the horizontal axis and the vertical microscope column (Fig.1). The original Philips CM30 column is highly modified with pressure limiting apertures around the beam and multiple stages of differential pumping (Fig.2).

ETEM provides facilities for dynamic *in-situ* experiments in an atomic resolution (<0.2nm) TEM under controlled conditions of gas/vapor environment at regular operating pressures up to ~50mbar, but usually rather less (depending on the experiment and the gas being used), and at selected and accurately known temperatures from –150°C to 1100°C, and in a few cases up to 2000°. Reviews of the important scientific impact of ETEM in solid state chemistry and related fields, including catalysis research, are provided by references 1 and 2.

A classic ETEM experiment (3) is illustrated in Figs.3-5. In this, we see the results of a carefully controlled increase in the temperature of the sample hot stage from 20°C (Fig.3a) to 575°C (Figs3b-5), in an atmosphere of a few mbar of air. The residual Ni-Co catalyst metal is extracted to the surface of the carbon nanotube bundles, and then coalesces into discrete particles (Figs 3b-5). In the corresponding lattice image (Fig.5) they are seen to form highly crystalline alloy particles with well ordered (111) planes, but still to wet the CNT bundle. The direct real space imaging in the electron microscope uniquely communicates the form and distribution of the particles in real time, allowing interactive control of the experiment and high productivity – in this case half a day rather than half a year *ex situ*.

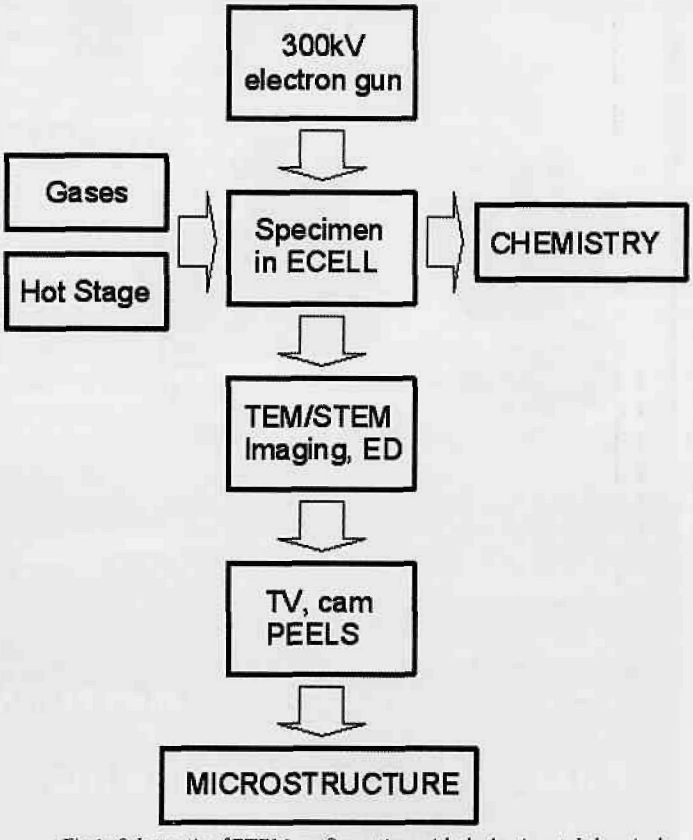

Fig.1 : Schematic of ETEM configuration with the horizontal chemical reactor (product chemistry) across the specimen chamber of the vertical microscope column (product microstructure) sharing the same hot stage sample in a controlled environment of gas/vapor/liquid.

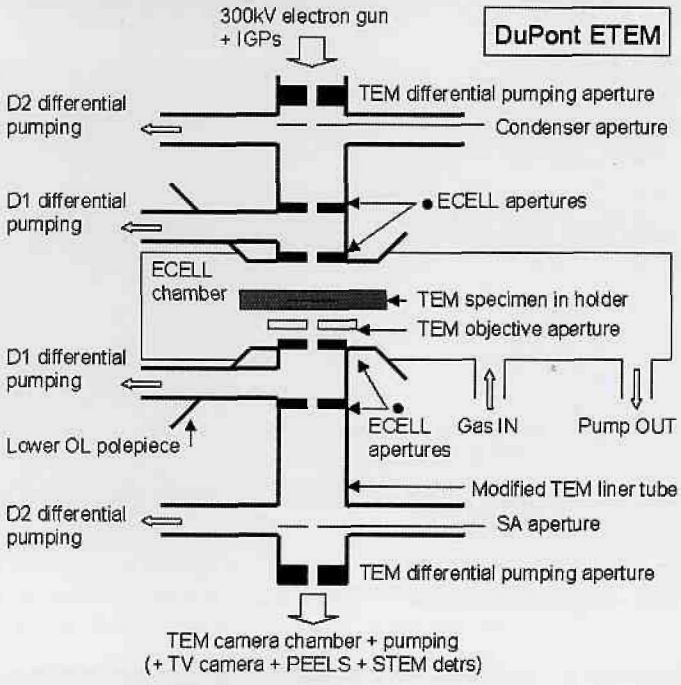

Fig.2 : Cross-section schematic of the ECELL section of the atomic resolution ETEM showing the ECELL apertures and multiple differential pumping lines added to the modified TEM column on either side (vertically) of the sample. A gate valve (not shown in this section) is added to protect the ion getter pump from the reaction species during ETEM operations. The key area containing the specimen in this very large instrument is <1ml in volume.

Of course, many *in-situ* experiments in regular high vacuum systems, including hot-stage studies of phase transformation, sintering, and inter-diffusion, have been very successful; and in some cases surprisingly so. One thinks of the brilliant results from the Sinclair group at Stanford (4) and there is a local example of highly informative impeded glass sintering SEM experiments in a regular high vacuum system (5) with excellent, and frankly at first unexpected, correlations with ex-situ furnace studies (over two years !) in an air atmosphere. However, for many applications with reactive materials, such as but not restricted to catalysts, data from transfer through air, or reaction and analysis of actually or potentially reactive substances in high vacuum environments at room temperature, are not very useful. In some cases, they can be downright misleading in providing meaningful knowledge relevant to the real world. There are obvious parallels with ESEM which the earliest ETEM work predates by several decades (6,7).

Dynamic *in-situ* experiments can be very efficient, and productive of data, in scanning a range of experimental conditions in a single session, and in mechanistic studies. Moreover, as is often the case in catalysis, the active phase is metastable with respect to temperature and environment, the key data for rational design of new materials can only be obtained from dynamic *in-situ* studies (1,2,6,7). The limits on the systems are a maximum gas pressure in the mbar range dictated by electron scattering and finally leakage into the gun. These *in-situ* conditions are generally adequate to ensure the reacting surface is flooded with the desired species. This is particularly important for some hot stage studies of oxides since a microscope vacuum has a tendency to be a reducing environment. Higher reaction or treatment pressures can be used with the beam turned off or in interconnected *ex-situ* chambers.

Environmental Transmission Electron Microscopy (ETEM) has been practiced since the middle of the last century (7) and modern

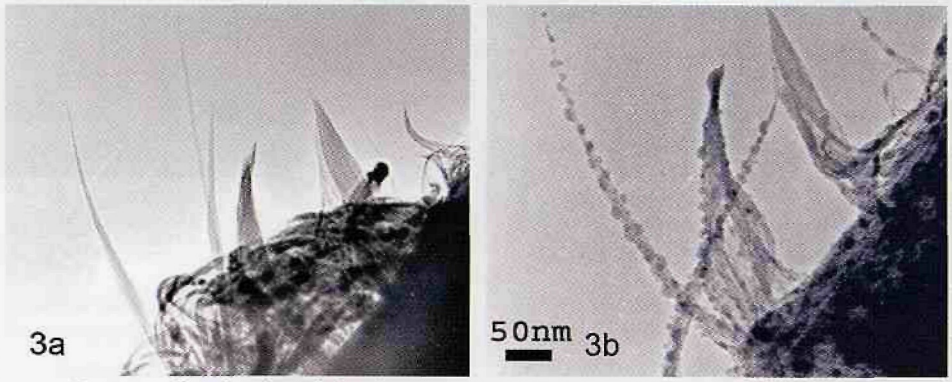

Fig.3 : Bundles of single walled carbon nanotubes (SWCNTs)
(a) at 20°C before reaction
(b) same area after reaction in a few mbar of air at 575°C to extract the residual Ni-Co alloy catalyst metal

ETEM systems (8) have most of the atomic image resolution and analytical capabilities of contemporary high vacuum instruments. The biggest remaining restriction is on EDX analysis, due to the fixed lower aperture and hot stage geometry and material limitations (and with lo-Z detectors limiting sample temperatures to <450°C). For the first few decades only old, or relatively poorly performing, instruments were converted temporarily to ETEM configurations. But when new high performance systems were used as the starting point for permanent conversions (8), many of the limitations were found to be due to the base systems rather than inherent in the ETEM components. Nevertheless, a number of major scientific studies were completed with the old systems using image resolutions of a few nanometers and classical diffraction contrast defect analysis (1,6). This is still a very effective, if a regrettably less practiced, methodology.

It is essential to ensure the effect of the electron beam is minimally invasive; in part by using lower electron beam doses and sensitive recording methods, and by rigorous audit of results with and without the electron beam on continuously. In any scientific study, a hot stage at controlled and accurately known temperatures should be used; rather than beam heating of indeterminate intensity, wide variations in local effect and mostly alien to the real world. Of course, a rigorous approach is demanded experimentally; especially to obtain the most informative continuous dynamic data from a small selected area or a feature at high resolution and magnification, as the environment, temperature or other controlled conditions are varied systematically. After the basic data are recorded they must always be confirmed in a rigorous comparison end-point experiment with the beam turned off during the reaction sequence, and used only for analysis at the end of the experiment. Data found to be influenced in any way by the electron beam are usually artefact and should be discarded. This is obviously very dependent on materials and conditions, but it seems to be a much bigger problem using electron beam energies above 200kV. ETEM can add valuable mechanistic and spatially resolved microstructure and defect data to wider studies, but must always be related to them.

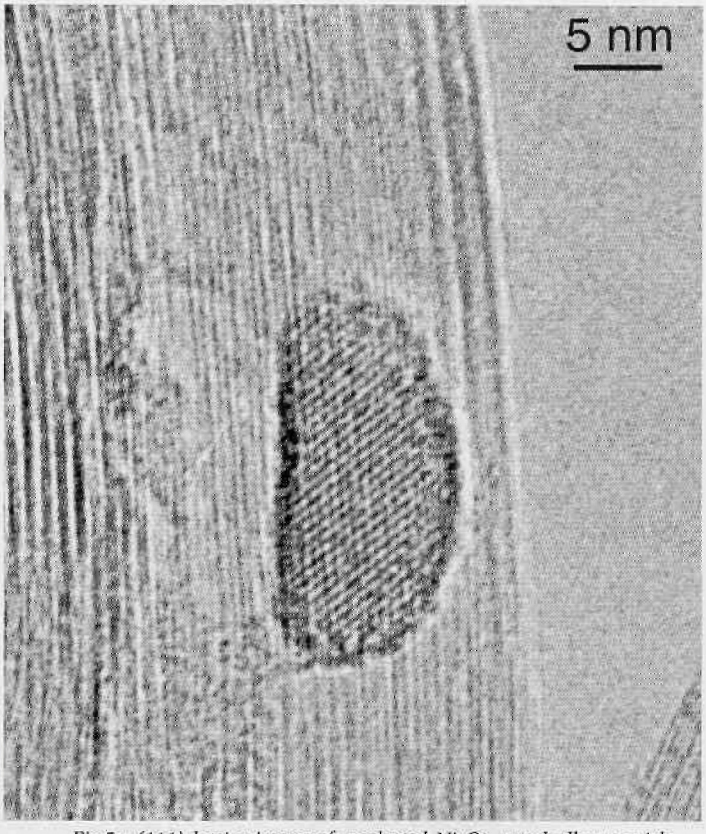

Fig.5 : (111) lattice image of a selected Ni-Co metal alloy particle extracted from the SWCNT matrix during the in-situ reaction sequence and recorded in an atmosphere of ~1mbar of air at the reaction temperature of 575°C. Scale bar is 5nm.

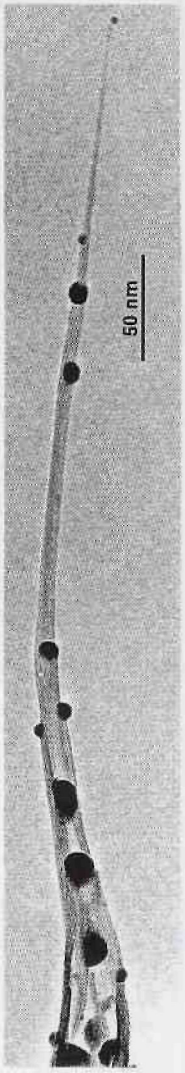

Fig. 4: The metal sinters into discrete Ni-Co metal particles and this shows the nanotubes can be purified, but other interactions may also be occurring. Scale bar is 50nm.

The basic configuration of the ETEM (Fig. 2) is a short (<10mm) path length of controlled environment with gas/vapor introduced, or in some cases with liquid injected onto the sample, and containing the microscope specimen in an otherwise high vacuum TEM column. The limited sample area is the only part of the system shared by both the chemical reactor stream and the microscope. The environment may be contained between thin windows (often in a special sample holder) or by differentially pumped apertures in the microscope; and sometimes with both. Windows are generally used for long term studies with liquids (9) and apertures for higher resolution gas/vapor studies. Early ETEM configurations in the modern era included both converted 100kV TEMs (Baker) and 1000kV HVEMs (Swann). See ref 7 for a good summary.

In the best earlier systems, differentially pumped apertures and pumping lines were inserted between the objective lens polepieces of the TEM. Alignment was always an issue and the required wide gap lens designs also limited resolution prior to the aberration correction proposed to reduce this problem in next generation systems.

Major improvements in the past decade or so have included keying the aperture assembly alignment, and more radically placing the apertures themselves, inside the polepiece bores with the first stage of differential pumping connected through lateral holes in the actual polepieces (Fig.2). With more efficient pumping lines, larger beam apertures (200-600um) can be used. This is necessary for adequate alignment, to open up the recordable diffraction angle and in the end to avoid limiting high resolution performance if the fixed apertures (below the sample for TEM, where it really matters, and in principle above it

for STEM and CBDP) are too small. The manufacturing tolerances on the centering of selected regular microscope apertures (<20um), and on machining tolerances for mounting them in a fixed alignment, are fully adequate for the purpose. In essence the modern ETEM became possible once these simple engineering facts were recognized and acted upon. In our designs (8) the regular adjustable objective aperture is retained inside the ETEM's ECELL section (Fig. 2) for its usual useful TEM functions. The latest developments of ETEM (10, 11) have an FEG and require additional stages of differential pumping added to the configuration described here (and on which they are based). Fortunately, the vacuum conditions in the modern ETEM (8) are significantly better than those in a regular TEM, greatly reducing the contamination issues critical for chemistry - and with which the ETEM apertures and gas flow can help even in older systems (A F Moodie and P L Gai, private communication).

We want to point out that any modifications to an electron microscope, and especially a higher voltage TEM column, must be undertaken with a well informed plan and rigorous procedures to ensure the outcome is at least as safe as the base instrument, especially with regard to potential x-ray emissions. We used a combination of innovative internal Al-shielded Ta x-ray beam stops and extensive additional external lead shielding, with stringent auditing of both design and implementation.

The emphasis in ETEM is on dynamic *in-situ* studies of reaction and other change mechanisms under controlled, near real world conditions of environment and temperature; with minimally invasive microscopy for analysis. Any compromises in TEM performance with the ETEM functionality added are now very limited. On a personal note, we were happy to find that although our custom prototype high resolution ETEM took significant time to plan in detail, the first lattice resolution images were achieved within a few minutes of first switching on the beam – with no magic required. In the future, aberration correction is expected to be very important in ETEM, in helping to simplify image interpretation, particularly between 0.1 and 0.25nm, improving imaging of small particle structures against a support background (12), and allowing the use of wider gap polepieces with space for more stage manipulations and other *in-situ* facilities such as straining. ■

Acknowledgements

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References

1. P L Gai, Cat Rev Sci Eng, 34 (1992) 1.
2. P L Gai and E D Boyes, "Electron Microscopy in Heterogeneous Catalysis, Institute of Physics Publ., Bristol, 2003.
3. P L Gai, G Lavin and E D Boyes, Electron Microscopy (Proc ICEM 14), publd, IOP, 3 (1998) 501.
4. R Sinclair, T Yamashita and F A Ponce, Nature 290 (1981) 386.
5. R Bordia, E D Boyes and A Jagota, Proc MRS, 249 (1992) 475.
6. P L Gai, E D Boyes and J D Bart, Phil Mag. A45 (1982) 531.
7. E P Butler and K F Hale, Dynamic Experiments in the EM, publd North Holland, Amsterdam 1981.
8. E D Boyes and P L Gai, Ultramicroscopy, 67 (1997) 219.
9. D D Double, A Hellawell and S J Perry, Proc Roy Soc A359 (1978) 435.
10. T W Hansen et al, Science 294 (2001) 1508.
11. V P Olesko et al, J Electron Microscopy 51 (2002) 527.
12. P L Gai et al, J Microscopy 142 (1986) 9.

* The ETEM definition was introduced by one of the authors, PLG, to codify previous less descriptive terms, including controlled environment (ECELL) TEM and gas atmosphere studies.

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